Introduction to density-functional theory

Robert van Leeuwen
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A. General properties

The Schrödinger equation for a general many-electron system with N electrons is given by

$$i\frac{\partial\psi}{\partial t}=\hat{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\Psi \tag{1}$$

The Hamiltonian in this equation

$$\hat{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\sum_{i=1}^{N}h(\mathbf{r}_i)+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} \tag{2}$$

where $h(\mathbf{r})$ is the one-body part of the Hamiltonian and where the last term describes the Coulombic repulsion between the electrons. The one-body part has the form

$$h(\mathbf{r})=-\frac{1}{2}\nabla^2+v(\mathbf{r}) \tag{3}$$

where the external potential $v(\mathbf{r})$ for a molecule is given by the sum of nuclear potentials

$$v(\mathbf{r})=-\sum_{m=1}^{M}\frac{Z_m}{|\mathbf{r}-\mathbf{R}_m|} \tag{4}$$

where the nuclei have charge Z_m and are located at positions $\mathbf{R}_m$. The many-electron wave function depends onboth space and spin coordinates

$$\Psi\equiv\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N,t) \tag{5}$$

where the spin variable σ can have only two values $\sigma=+1,-1$ or $\sigma=\uparrow,\downarrow$ (up/down). According to the Pauli principle the wave function must be *anti-symmetric* for the case of fermions i.e.

$$\Psi(\ldots\mathbf{r}_i\sigma_i\ldots\mathbf{r}_j\sigma_j\ldots)=-\Psi(\ldots\mathbf{r}_j\sigma_j\ldots\mathbf{r}_i\sigma_i\ldots) \tag{6}$$

In particular this means that no two electrons can have the same space-spin variables:

$$\Psi(\ldots\mathbf{r}_i\sigma_i\ldots\mathbf{r}_i\sigma_i\ldots)=0 \tag{7}$$

The anti-symmetry of the many-electron wavefunction means that electrons are fundamentally indistinguishable. We have the following probability interpretation. the quantity

$$|\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N,t)|^2\,d^3\mathbf{r}_1d^3\mathbf{r}_2\ldots d^3\mathbf{r}_N \tag{8}$$

is the probability to find an electron in volume element $d^3\mathbf{r}_1$ around $\mathbf{r}_1$ with spin σ_1, and to find an electron in volume element $d^3\mathbf{r}_2$ around $\mathbf{r}_2$ with spin σ_2, etc... Since the total probability must integrate to one we have the condition

$$\sum_{\sigma_1\ldots\sigma_N}\int d^3\mathbf{r}_1d^3\mathbf{r}_2\ldots d^3\mathbf{r}_N|\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N,t)|^2\;=1 \tag{9}$$

B. Ground state and Rayleigh-Ritz principle

Let us first consider stationary systems in which the Hamiltonian is time-independent. For such systems we can write

$$\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N,t) = e^{iE_jt}\Psi_j(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N) \tag{10}$$

where the Ψ_j are the eigenfunctions of the time-independent Schrödinger equation.

$$\hat{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\Psi_j(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N) = E_j\Psi_j(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N) \tag{11}$$

We define a *ground state* Ψ_0 to be a state with the lowest possible energy, i.e.

$$E_0 \leq E_j \quad \forall\, j \tag{12}$$

There could be several linearly independent wave functions with the lowest energy. If this is the case the ground state is called *degenerate*. This happens for instance in open shell atoms. When the ground state is unique (up to a trivial phase factor $e^{i\alpha}$) the ground state is called *nondegenerate*.

The many-body wave functions are part of a many-body Hilbert space (normed, complete space) with inner product

$$\langle\Psi|\Phi\rangle = \sum_{\sigma_1\ldots\sigma_N}\int d^3\mathbf{r}_1 d^3\mathbf{r}_2\ldots d^3\mathbf{r}_N\;\Psi^*(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)\Phi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N) \tag{13}$$

The Hamiltonian is a hermitian operator

$$\langle\Phi|\hat{H}|\Psi\rangle = \langle\Psi|\hat{H}|\Phi\rangle^* \tag{14}$$

and consequently the eigenfunctions Ψ_i of the Hamiltonian form a complete othornormal set with respect to Hilbert space inner prduct. This means that any state Ψ in the Hilbert space can be expressed as a linear combination of them, i.e. for any Ψ we can write

$$\Psi = \sum_i c_i\,\Psi_i \tag{15}$$

where, since $\langle\Psi_i|\Psi_j\rangle = \delta_{ij}$, it is easy to see that when Ψ is normalized to one that

$$\sum_i |c_i|^2 = 1 \tag{16}$$

Then we also see that

$$\langle\Psi|\hat{H}|\Psi\rangle = \sum_{i,j} c_i^* c_j\,\langle\Phi_i|\hat{H}|\Psi_j\rangle = \sum_{i,j} E_i|c_i|^2 \geq E_0\sum_i |c_i|^2 = E_0 \tag{17}$$

where we used that $E_i \geq E_0$. So we obtain that the expectation value of the Hamiltonian of any normalized state, $\langle\Psi|\Psi\rangle = 1$, has a lower bound given by the ground state energy of the Hamiltonian, i.e.

$$\langle\Psi|\hat{H}|\Psi\rangle \geq E_0 \tag{18}$$

This is the Rayleigh-Ritz principle. We can make this statement more precise. Suppose the ground state is degenerate and we have q degenerate states $\{\Psi_1\ldots\Psi_q\}$. Then we see that

$$\langle\Psi|\hat{H}|\Psi\rangle = E_0\sum_{i=1}^{q}|c_i|^2 + \sum_{i>q}|c_i|^2\,E_i = E_0 + \sum_{i>q}|c_i|^2(E_i - E_0) \tag{19}$$

Since $E_i > E_0$ for $i > q$ we see that $\langle\Psi|\hat{H}|\Psi\rangle = E_0$ only when $c_i = 0$ for $i > q$. So only a linear combination of ground states can give expectation value equal to E_0.

C. Densities and density matrices

To calculate the energy of a many-particle system with two-body interactions we do not need to know the full many-body wave function. We can get along with reduced quantities. As an example we start with the one-body potential energy

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i) \tag{20}$$

Its expectation value is given by

$$\begin{aligned}\langle \Psi | \hat{V} | \Psi \rangle &= \sum_{i=1}^{N} \sum_{\sigma_1 \dots \sigma_N} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N v(\mathbf{r}_i) |\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)|^2 \\ &= N \sum_{\sigma_1 \dots \sigma_N} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N v(\mathbf{r}_1) |\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)|^2 \\ &= \int d^3\mathbf{r}_1 \, n(\mathbf{r}_1) v(\mathbf{r}_1) \end{aligned} \tag{21}$$

where in the second line we used the symmetry of $|\Psi|^2$ under permutation of spin-space variables and in the last line defined the electron density $n(\mathbf{r})$ by the equation

$$n(\mathbf{r}_1) = N \sum_{\sigma_1 \dots \sigma_N} \int d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N |\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)|^2 \tag{22}$$

In this expression we integrate over all spatial variables except coordinate $\mathbf{r}_1$. So we obtained the result that the potential energy can be calculated from the knowledge of the density alone:

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d^3\mathbf{r} \, n(\mathbf{r}) v(\mathbf{r}) \tag{23}$$

Taking the special case $v(\mathbf{r}) = \delta(\mathbf{r}_0 - \mathbf{r})$ we see from Eq.(20) and Eq.(23)that

$$\langle \Psi | \sum_{i=1}^{N} \delta(\mathbf{r}_0 - \mathbf{r}_i) | \Psi \rangle = n(\mathbf{r}_0) \tag{24}$$

We can therefore define the density operator as

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{25}$$

The expectation value of this operator then gives the density

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \tag{26}$$

We can also now rewrite Eq.(20) as

$$\hat{V} = \int d^3\mathbf{r} \, \hat{n}(\mathbf{r}) v(\mathbf{r}) = \sum_{i=1}^{N} v(\mathbf{r}_i) \tag{27}$$

We can go through a similar procedure for the kinetic energy

$$\hat{T} = \sum_{i}^{N} -\frac{1}{2} \nabla_i^2 \tag{28}$$

The result of this calculation is

$$\langle\Psi|\hat{T}|\Psi\rangle = -\frac{1}{2}\int d^3\mathbf{r}' \left[\nabla'^2\gamma(\mathbf{r},\mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'} \tag{29}$$

where we defined the one-particle density matrix as

$$\gamma(\mathbf{r},\mathbf{r}') = N\sum_{\sigma_1\ldots\sigma_N}\int d^3\mathbf{r}_2\ldots d^3\mathbf{r}_N\,\Psi^*(\mathbf{r}\sigma_1,\ldots,\mathbf{r}_N\sigma_N)\Psi(\mathbf{r}'\sigma_1,\ldots,\mathbf{r}_N\sigma_N) \tag{30}$$

Exercise: Prove relation (29).

The one-particle density matrix is dependent of two coordinates and therefore a more nonlocal object than the density. From the density can be calculated as

$$n(\mathbf{r}) = \gamma(\mathbf{r},\mathbf{r}) \tag{31}$$

as follows directly from the definition of γ. finally, for two-particle interactions of the form

$$\hat{W} = \frac{1}{2}\sum_{i\neq j} w(\mathbf{r}_i,\mathbf{r}_j) \tag{32}$$

(the Coulomb potential corresponds to $w(\mathbf{r},\mathbf{r}') = 1/|\mathbf{r}-\mathbf{r}'|$ one has

$$\langle\Psi|\hat{W}|\Psi\rangle = \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}'\,\Gamma(\mathbf{r},\mathbf{r}')w(\mathbf{r},\mathbf{r}') \tag{33}$$

where we defined the diagonal two-particle density matrix as

$$\Gamma(\mathbf{r},\mathbf{r}') = N(N-1)\sum_{\sigma_1\ldots\sigma_N}\int d^3\mathbf{r}_3\ldots d^3\mathbf{r}_N|\Psi(\mathbf{r}\sigma_1,\mathbf{r}'\sigma_2,\mathbf{r}_3\sigma_3,\ldots,\mathbf{r}_N\sigma_N)|^2 \tag{34}$$

i.e. we integrate over all coordinates except the first two arguments.

Exercise: Prove relation (33).

If we take the special case $w(\mathbf{r},\mathbf{r}') = \delta(\mathbf{x}-\mathbf{r})\delta(\mathbf{y}-\mathbf{r}')$ then we see from Eq.(32) and (33) that we have

$$\langle\Psi|\sum_{i\neq j}\delta(\mathbf{x}-\mathbf{r}_i)\delta(\mathbf{y}-\mathbf{r}_j)|\Psi\rangle = \Gamma(\mathbf{x},\mathbf{y}) \tag{35}$$

We can therefore define the operator $\hat{\Gamma}(\mathbf{r},\mathbf{r}')$

$$\hat{\Gamma}(\mathbf{r},\mathbf{r}') = \sum_{i\neq j}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \tag{36}$$

which has the property that

$$\Gamma(\mathbf{r},\mathbf{r}') = \langle\Psi|\hat{\Gamma}(\mathbf{r},\mathbf{r}')|\Psi\rangle \tag{37}$$

If we now combine our results then we see that the total energy of the system is given by the expression

$$E = -\frac{1}{2}\int d^3\mathbf{r}' \left[\nabla'^2\gamma(\mathbf{r},\mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'} + \int d^3\mathbf{r}\,n(\mathbf{r})v(\mathbf{r}) + \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}'\,\Gamma(\mathbf{r},\mathbf{r}')w(\mathbf{r},\mathbf{r}') \tag{38}$$

Therefore to calculate the total energy we only need to know $\gamma(\mathbf{r},\mathbf{r}')$ and $\Gamma(\mathbf{r},\mathbf{r}')$ (since the density is obtained as $n(\mathbf{r})=\gamma(\mathbf{r},\mathbf{r})$). All the objects that we defined sofar are special case of the p-particle density matrix $\Gamma^{(p)}$ defined as

$$\Gamma^{(p)}(\mathbf{r}_1\ldots\mathbf{r}_p;\mathbf{r}'_1\ldots\mathbf{r}'_p)=\frac{N!}{(N-p)!} \tag{39}$$
$$\times\sum_{\sigma_1\ldots\sigma_N}\int d^3\mathbf{r}_{p+1}\ldots d^3\mathbf{r}_N\Psi^*(\mathbf{r}_1\sigma_1,\ldots\mathbf{r}_p\sigma_p,\mathbf{r}_{p+1}\sigma_{p+1}\ldots\mathbf{r}_N\sigma_N)\Psi(\mathbf{r}'_1\sigma_1,\ldots\mathbf{r}'_p\sigma_p,\mathbf{r}_{p+1}\sigma_{p+1}\ldots\mathbf{r}_N\sigma_N)$$

In particular we have

$$n(\mathbf{r}) = \Gamma^{(1)}(\mathbf{r},\mathbf{r}) \tag{40}$$
$$\gamma(\mathbf{r},\mathbf{r}') = \Gamma^{(1)}(\mathbf{r},\mathbf{r}') \tag{41}$$
$$\Gamma(\mathbf{r},\mathbf{r}') = \Gamma^{(2)}(\mathbf{r},\mathbf{r}';\mathbf{r},\mathbf{r}') \tag{42}$$

In fact all objects can be calculated from the two-particle density matrix since

$$(N-1)\gamma(\mathbf{r},\mathbf{r}')=\int d^3\mathbf{r}''\,\Gamma^{(2)}(\mathbf{r},\mathbf{r}'';\mathbf{r},\mathbf{r}'') \tag{43}$$

So we can conclude that to calculate the energy of a many-body system with two-particle interactions we do not need the full many-body wave function. All we need is the two-particle density matrix. We finally note a special case of Eq.(43) that will be useful later. If we take $\mathbf{r}=\mathbf{r}'$ in Eq.(43) we obtain the relation

$$(N-1)n(\mathbf{r})=\int d^3\mathbf{r}'\,\Gamma(\mathbf{r},\mathbf{r}') \tag{44}$$

where Γ is the diagonal two-particle density matrix.

D. Noninteracting particles

To get some insight into the structure of many-particle wave functions and density matrices we consider the case of noninteracting particles. The Hamiltonian is then given by

$$\hat{H}=\hat{T}+\hat{V}=\sum_{i=1}^{N}h(\mathbf{r}_i) \tag{45}$$

where

$$h(\mathbf{r})=-\frac{1}{2}\nabla^2+v(\mathbf{r}) \tag{46}$$

Let us start with the case of one particle. Then the Schrödinger equation is simply given by

$$h(\mathbf{r})\psi_i(\mathbf{r}\sigma)=\epsilon_i\psi_i(\mathbf{r}\sigma) \tag{47}$$

Since the Hamiltonian does not depend on spin we can separate space and spin coordinates and write $\psi_i(\mathbf{r})=\phi_i(\mathbf{r})\zeta_i(\sigma)$ where $\zeta_i(\sigma)$ is a spin function and $\phi(\mathbf{r})$ is a spatial wave function that satisfies the equation

$$h(\mathbf{r})\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}) \tag{48}$$

Since the spin coordinate can attain only two values every spin function $\zeta(\sigma)$ can be written as a linear combination of an up and a down spin function, i.e.

$$\zeta(\sigma) = c_1\alpha(\sigma) + c_2\beta(\sigma) \tag{49}$$

with $|c_1|^2 + |c_2|^2 = 1$ and where $\alpha(\sigma)$ and $\beta(\sigma)$ are defined as

$$\alpha(\sigma) = \delta_{\sigma,\uparrow} \tag{50}$$

$$\beta(\sigma) = \delta_{\sigma,\downarrow} \tag{51}$$

Let us now consider the case of two particles. The Hamiltonian is given by

$$\hat{H} = h(\mathbf{r}_1) + h(\mathbf{r}_2) \tag{52}$$

If we now introduce the short notation $\mathbf{x} = (\mathbf{r}\sigma)$ for a space-spin coordinate then we need to find an anti-symmetric two-particle wave function :

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1) \tag{53}$$

One can check that a possible normalized solution is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}(\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2) - \phi_j(\mathbf{x}_1)\phi_i(\mathbf{x}_2)) \tag{54}$$

where the orbitals $\phi_i(\mathbf{x})$ are eigenstates to the one-particle Schrödinger equation

$$h(\mathbf{r})\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x}) \tag{55}$$

This is readily verified. We have that

$$\begin{aligned} (h(\mathbf{r}_1) + h(\mathbf{r}_2))\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2) &= (h(\mathbf{r}_1)\phi_i(\mathbf{x}_1))\phi_j(\mathbf{x}_2) + \phi_i(\mathbf{x}_1)(h(\mathbf{r}_2)\phi_j(\mathbf{x}_2)) \\ &= \epsilon_i\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2) + \epsilon_j\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2) \\ &= (\epsilon_i + \epsilon_j)\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2) \end{aligned} \tag{56}$$

and of course similarly for the product with i and j interchanged. We therefore indeed see that

$$(h(\mathbf{r}_1) + h(\mathbf{r}_2))\Psi(\mathbf{x}_1, \mathbf{x}_2) = E\Psi(\mathbf{x}_1, \mathbf{x}_2) \tag{57}$$

where $E = \epsilon_i + \epsilon_j$. This wave function is a so-called Slater determinant and can be written as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_i(\mathbf{x}_1) & \phi_i(\mathbf{x}_2) \\ \phi_j(\mathbf{x}_1) & \phi_j(\mathbf{x}_2) \end{vmatrix} \tag{58}$$

It describes a configuration of two particles in which in particle is in level i and another one in level j. The ground state is obtained by putting both particles in the lowest energy level. But then the orbitals cannot have the same spin functions. We can choose

$$\phi_1(\mathbf{x}) = \varphi_0(\mathbf{r})\delta_{\sigma,\uparrow} \tag{59}$$

$$\phi_2(\mathbf{x}) = \varphi_0(\mathbf{r})\delta_{\sigma,\downarrow} \tag{60}$$

where $\varphi_0(\mathbf{r})$ is the lowest state of the hamiltonian $h(\mathbf{r})$, i.e.

$$h(\mathbf{r})\varphi_0(\mathbf{r}) = \epsilon_0\varphi_0(\mathbf{r}) \tag{61}$$

Then the Slater determinant wave function has the form

$$\begin{aligned}\Psi(\mathbf{x}_1,\mathbf{x}_2) &= \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_0(\mathbf{r}_1)\delta_{\sigma_1,\uparrow} & \varphi_0(\mathbf{r}_2)\delta_{\sigma_2,\uparrow}\\ \varphi_0(\mathbf{r}_1)\delta_{\sigma_1,\downarrow} & \varphi_0(\mathbf{r}_2)\delta_{\sigma_2,\downarrow}\end{vmatrix}\\ &= \varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2)\frac{1}{\sqrt{2}}(\delta_{\sigma_1,\uparrow}\delta_{\sigma_1,\downarrow}-\delta_{\sigma_1,\downarrow}\delta_{\sigma_1,\uparrow})\\ &= \varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2)\theta(\sigma_1,\sigma_2) \qquad (62)\end{aligned}$$

where we defined the spin function

$$\theta(\sigma_1,\sigma_2)=\frac{1}{\sqrt{2}}(\delta_{\sigma_1,\uparrow}\delta_{\sigma_1,\downarrow}-\delta_{\sigma_1,\downarrow}\delta_{\sigma_1,\uparrow}) \qquad (63)$$

which corresponds to a two-particle spin function (corresponding to a singlet state with $S=S_z=0$). The ground state energy of this two-particle system is $E=2\epsilon_0$.

With all these preparations it should now be easy to guess a form for the wave function of N particles. It is given by

$$\begin{aligned}\Psi(\mathbf{x}_1\ldots\mathbf{x}_N) &= \frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_{i_1}(\mathbf{x}_1) & \ldots & \phi_{i_1}(\mathbf{x}_N)\\ \vdots & & \vdots\\ \phi_{i_N}(\mathbf{x}_1) & \ldots & \phi_{i_N}(\mathbf{x}_N)\end{vmatrix}\\ &= \frac{1}{\sqrt{N!}}\sum_{\pi}(\operatorname{sgn}\pi)\phi_{i_{\pi(1)}}(\mathbf{x}_1)\ldots\phi_{i_{\pi(N)}}(\mathbf{x}_N) \qquad (64)\end{aligned}$$

where π runs over all permutations of the variables $(1\ldots N)$ and $\operatorname{sgn}\pi$ is the sign of the permutation. For this wave function the eigenenergy is given by

$$E=\epsilon_{i_1}+\epsilon_{i_2}+\ldots+\epsilon_{i_N} \qquad (65)$$

The Slater determinant with orbitals $\phi_{i_1}\ldots\phi_{i_N}$ is often written as

$$\Psi=|i_1\ldots i_N\rangle \qquad (66)$$

One can easily show that the Slater determinants are orthonormal

$$\langle i_1\ldots i_N|j_1\ldots j_N\rangle=\delta_{i_1j_1}\delta_{i_2j_2}\ldots\delta_{i_Nj_N} \qquad (67)$$

Exercise: Find explicit expressions for $\gamma(\mathbf{r},\mathbf{r}')$, $n(\mathbf{r})$, and $\Gamma(\mathbf{r},\mathbf{r}')$ in terms of the orbitals $\phi_{i_1}\ldots\phi_{i_N}$ for the case that Ψ is a Slater determinant $\Psi=|i_1\ldots i_N\rangle$.

III. THE HOHENBERG-KOHN THEOREM

A. The Hohenberg-Kohn mappings

We have seen that the energy of a many-particle system can be calculated from knowledge of the two-particle density matrix. We are now going to prove a stronger statement. The ground state observables (like the total energy) of a many-particle system with a nondegenerate ground state are determined by the ground state density $n(\mathbf{r})$ alone. How can we show this? If we have a general external potential

$$\hat{V}=\sum_{i=1}^{N}v(\mathbf{r}_i) \qquad (68)$$

then clearly the ground state wave function (for fixed kinetic energy $\hat{T}$ and interaction $\hat{W}$) is a functional of the external potential v by means of solution of the Schrödinger equation

$$(\hat{T} + \hat{V} + \hat{W})\Psi[v] = E[v]\Psi[v] \tag{69}$$

The square brackets here denote that we are dealing with objects depending on a function, i.e. functionals. For instance, the ground state energy $E[v]$ is a number depending on the function $v(\mathbf{r})$ and thereby a functional of the potential.
We will now prove that the potential (apart from an arbitrary constant or gauge) is completely determined by the ground state density. This theorem is known as the Hohenberg-Kohn theorem and forms the foundation of density functional theory. We will for the moment consider only nondegenerate ground states. The proof of this statement proceeds in two steps. For this we consider two mappings. We consider a mapping $C : \mathcal{V} \to \mathbf{\Psi}$ from the set of potentials $\mathcal{V}$ to the set of ground state wavefunctions $\mathbf{\Psi}$ and we consider a mapping $D : \mathbf{\Psi} \to \mathcal{N}$ from the set of ground state wave functions to the set of ground state densities $\mathcal{N}$ to belong to it. The the proof proceeds in two steps. In step 1 we prove that C is invertible and in step 2 we prove that D is invertible.

Step 1 : There is a 1-1 correspondence between potentials and ground state wavefunctions, i.e. map C is invertible.

Proof. We first establish some nomenclature. We will call two potentials different if they differ more than a constant, i.e. $v_1 \neq v_2 + C$. It is clear that two potentials that differ only by an overall constant give identical ground state wave functions. We will also call two wavefunctions different if they differ more than a trivial phase factor $\Psi_1 \neq e^{i\alpha}\Psi_2\,(\alpha \in \mathbb{R})$. The proof proceeds by *reductio ad absurdum.* Suppose that map C is not invertible. Then there are two different ($v_1 \neq v_2 + C$) potentials that yield the same ground state Ψ and consequently we have

$$\hat{H}_1\Psi = (\hat{T} + \hat{V}_1 + \hat{W})\Psi = E_1\Psi \tag{70}$$

$$\hat{H}_2\Psi = (\hat{T} + \hat{V}_2 + \hat{W})\Psi = E_2\Psi \tag{71}$$

Subtraction of both equations then gives

$$(\hat{V}_1 - \hat{V}_2)\Psi = (E_1 - E_2)\Psi = C\Psi \tag{72}$$

where C is a constant. If Ψ does not vanish on a set of measure zero (which it does not for potentials that do not contain infinite barriers) then we can divide out the wave functions and we obtain $\hat{V}_1 = \hat{V}_2 + C$, in contradiction with our assumption. Therefore our assumption must have been wrong and the map C must be invertible.

Step 2 : There is a 1-1 correspondence between nondegenerate ground state wave functions and ground state densities, i.e. the map D is invertible.

Proof. The proof proceeds again by the same *reductio ad absurdum* procedure. Suppose that map D is not invertible. Then there are two different wavefunctions that produce the same ground state density. Then

$$\begin{aligned} E_1 &= \langle\Psi_1|\hat{H}_1|\Psi_1\rangle = \langle\Psi_1|\hat{H}_2 + \hat{V}_1 - \hat{V}_2|\Psi_1\rangle = \langle\Psi_1|\hat{H}_2|\Psi_1\rangle + \int d^3\mathbf{r}\, n(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r})) \\ &> E_2 + \int d^3\mathbf{r}\, n(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r})) \end{aligned} \tag{73}$$

Similarly, by interchanging indices 1 and 2 we obtain

$$E_2 > E_1 + \int d^3\mathbf{r}\, n(\mathbf{r})(v_2(\mathbf{r}) - v_1(\mathbf{r})) \tag{74}$$

Adding these two equations then leads to the contradiction $E_1 + E_2 > E_1 + E_2$. Therefore our assumption must have been wrong and the map D must be invertible.

We have therefore proven that maps C and D are invertible. Consequently the combined map $D \circ C$ is invertible. This implies that there is a 1-1 correspondence between densities and potentials.

B. The Hohenberg-Kohn variational principle

So we established that the potential $v[n](\mathbf{r})$ is a functional of the ground state density $n(\mathbf{r})$. But then, by solution of the Schrödinger equation, also the ground state wavefunction is a functional $\Psi[n]$ and therefore the expectation value of any ground state observable $\hat{O}$

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle \tag{75}$$

is a functional of of the density. In particular we have that (for a fixed potential v_0) the ground state energy is a functional of the density:

$$\begin{aligned} E_{v_0}[n] &= \langle \Psi[n] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n] \rangle = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle + \int d^3\mathbf{r}\, n(\mathbf{r}) v_0(\mathbf{r}) \\ &= F_{\mathrm{HK}}[n] + \int d^3\mathbf{r}\, n(\mathbf{r}) v_0(\mathbf{r}) \end{aligned} \tag{76}$$

Here we defined the Hohenberg-Kohn functional $F_{\mathrm{HK}}[n]$ by the equation

$$F_{\mathrm{HK}}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle \tag{77}$$

This functional is independent of the external potential and therefore the same for all systems with Coulombic interparticle interactions, i.e. in this sense it is a *universal* functional. Let E_0 be the ground state energy and n_0 be the ground state potential of a system with external potential v_0 the obviously

$$E_{v_0}[n] = \langle \Psi[n] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n] \rangle > E_0 \quad \text{if } n \neq n_0 \tag{78}$$

Therefore the ground state density n_0 is obtained by minimizing the functional $E_{v_0}[n]$ over all densities for a fixed v_0. The minimum is obtained for the density that satisfies

$$\frac{\delta E_{v_0}[n]}{\delta n(\mathbf{r})} = 0 \tag{79}$$

or equivalently from the equation

$$\frac{\delta F_{\mathrm{HK}}[n]}{\delta n(\mathbf{r})} = -v_0(\mathbf{r}) \tag{80}$$

In this equation the density potential maping becomes clear. On the right hand side we specify the external potential v_0 of the system of interest and on the left hand side we have a determining equation that yields a density as an output.

IV. THE KOHN-SHAM CONSTRUCTION

A. Derivation of the Kohn-Sham equations

According to the Hohenberg-Kohn theorem there is a 1-1 relation between potentials and ground state densities. In particular, since the proof of the Hohenberg-Kohn theorem did not involve any special properties of the two-particle interaction, the proof is valid for noninteracting systems. Let us therefore consider a noninteracting systems with Hamiltonian $\hat{H}_s$ (s=single particle) and ground state density $n(\mathbf{r})$. We denote the external potential with $\hat{V}_s$ which we know , by the HK theorem, to be a functional of the density. We have

$$\hat{H}_s = \hat{T} + \hat{V}_s[n] \tag{81}$$

with grounds state wave function $\Phi_s[n]$ that satisfies

$$\begin{aligned} \hat{H}_s\Phi_s[n] &= E_s\Phi_s[n] && (82)\\ n(\mathbf{r}) &= \langle\Phi_s[n]|\hat{n}(\mathbf{r})|\Phi_s[n]\rangle && (83) \end{aligned}$$

The ground state wave function can be written as a Slater determinant

$$\begin{aligned} \Phi_s[n](\mathbf{x}_1\ldots\mathbf{x}_N) &= \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\mathbf{x}_1) & \ldots & \phi_1(\mathbf{x}_N) \\ \vdots & & \vdots \\ \phi_N(\mathbf{x}_1) & \ldots & \phi_N(\mathbf{x}_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}}\sum_\pi (\operatorname{sgn}\pi)\phi_{\pi(1)}(\mathbf{x}_1)\ldots\phi_{\pi(N)}(\mathbf{x}_N) && (84) \end{aligned}$$

This noninteracting system with density n and Hamiltonian $\hat{H}_s$ is called the Kohn-Sham (KS) system. The determinant Φ_s is called the Kohn-Sham wave function and the orbitals $\phi_i(\mathbf{x})$ are called the Kohn-Sham orbitals. The equations for the Kohn-Sham system can also be written as single-particle equations

$$\begin{aligned} \big(-\frac{1}{2}\nabla^2 \; + \; v_s(\mathbf{r})\big)\phi_i(\mathbf{r}\sigma) &= \epsilon_i\phi_i(\mathbf{r}\sigma) && (85)\\ n(\mathbf{r}) \; &= \; \sum_\sigma\sum_{i=1}^N |\phi_i(\mathbf{r}\sigma)|^2 && (86) \end{aligned}$$

For a spin-compensated systems, i.e. a system for which

$$\phi_1(\mathbf{x})\ldots\phi_N(\mathbf{x}) = \varphi_1(\mathbf{r})\delta_{\sigma,\uparrow}, \varphi_1(\mathbf{r})\delta_{\sigma,\downarrow}, \ldots\varphi_{N/2}(\mathbf{r})\delta_{\sigma,\uparrow}, \varphi_{N/2}(\mathbf{r})\delta_{\sigma,\downarrow} \tag{87}$$

we can write the KS equations as

$$\begin{aligned} \big(-\frac{1}{2}\nabla^2 \; + \; v_s(\mathbf{r})\big)\varphi_i(\mathbf{r}) &= \epsilon_i\varphi_i(\mathbf{r}) && (88)\\ n(\mathbf{r}) \; &= \; 2\sum_{i=1}^{N/2} |\varphi_i(\mathbf{r})|^2 && (89) \end{aligned}$$

The total energy of the KS is given by

$$E_s[n] = \langle\Phi_s[n]|\hat{T} + \hat{V}_s|\Phi_s[n]\rangle = T_s[n] + \int d^3\mathbf{r}\, n(\mathbf{r})v_s(\mathbf{r}) = \sum_{i=1}^N \epsilon_i \tag{90}$$

Here we defined the kinetic energy of a noninteracting system of density n as

$$\begin{aligned} T_s[n] \; &= \; \langle\Phi_s[n]|\hat{T}|\Phi_s[n]\rangle = \sum_\sigma\sum_{i=1}^N -\frac{1}{2}\int d^3\mathbf{r}\phi_i^*(\mathbf{r}\sigma)\nabla^2\phi_i(\mathbf{r}\sigma) \\ &= \; \sum_\sigma\sum_{i=1}^N \frac{1}{2}\int d^3\mathbf{r}\,|\nabla\phi_i(\mathbf{r}\sigma)|^2 && (91) \end{aligned}$$

Since $T_s[n]$ is a well-defined functional we can now define the exchange-correlation functional by the expression

$$E_{\mathrm{xc}}[n] \equiv F_{\mathrm{HK}}[n] - E_{\mathrm{H}}[n] - T_s[n] \tag{92}$$

where $E_{\mathrm{H}}[n]$ is the Hartree energy defined as

$$E_{\mathrm{H}}[n] = \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}'\, n(\mathbf{r})n(\mathbf{r}')w(\mathbf{r},\mathbf{r}') \tag{93}$$

With this definition the functional $F_{\mathrm{HK}}[n]$ can be split as

$$F_{\mathrm{HK}}[n] = T_s[n] + \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}'\, n(\mathbf{r})n(\mathbf{r}')w(\mathbf{r},\mathbf{r}') + E_{\mathrm{xc}}[n] \tag{94}$$

If we insert this expression into the variational equation Eq.(80) we obtain

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{\mathrm{H}}[n](\mathbf{r}) + v_{\mathrm{xc}}[n](\mathbf{r}) = -v_0(\mathbf{r}) \tag{95}$$

where we defined the Hartree and exchange-correlation potentials by the equations

$$\begin{aligned} v_{\mathrm{H}}[n](\mathbf{r}) &= \int d^3\mathbf{r}'\, n(\mathbf{r}')w(\mathbf{r},\mathbf{r}') && (96) \\ v_{\mathrm{xc}}[n](\mathbf{r}) &= \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} && (97) \end{aligned}$$

To make Eq.(95) more explicit we have to calculate the derivative $\delta T_s/\delta n(\mathbf{r})$. This is readily done as follows:

$$\begin{aligned} \frac{\delta T_s}{\delta n(\mathbf{r})} &= \frac{\delta}{\delta n(\mathbf{r})}\langle\Phi_s|\hat{T}|\Phi_s\rangle = \langle\frac{\delta\Phi_s}{\delta n(\mathbf{r})}|\hat{T}|\Phi_s\rangle + \langle\Phi_s|\hat{T}|\frac{\delta\Phi_s}{\delta n(\mathbf{r})}\rangle \\ &= \langle\frac{\delta\Phi_s}{\delta n(\mathbf{r})}|\hat{H}_s - \hat{V}_s|\Phi_s\rangle + \langle\Phi_s|\hat{H}_s - \hat{V}_s|\frac{\delta\Phi_s}{\delta n(\mathbf{r})}\rangle \\ &= E_s\Big(\langle\frac{\delta\Phi_s}{\delta n(\mathbf{r})}|\Phi_s\rangle + \langle\Phi_s|\frac{\delta\Phi_s}{\delta n(\mathbf{r})}\rangle\Big) \\ &\quad - \int d^3\mathbf{r}'\, v_s(\mathbf{r}')\Big(\langle\frac{\delta\Phi_s}{\delta n(\mathbf{r})}|\hat{n}(\mathbf{r}')|\Phi_s\rangle + \langle\Phi_s|\hat{n}(\mathbf{r}')|\frac{\delta\Phi_s}{\delta n(\mathbf{r})}\rangle\Big) \\ &= E_s\frac{\delta}{\delta n(\mathbf{r})}\langle\Phi_s|\Phi_s\rangle - \int d^3\mathbf{r}' v_s(\mathbf{r}')\frac{\delta}{\delta n(\mathbf{r})}\langle\Phi_s|\hat{n}(\mathbf{r}')|\Phi_s\rangle \\ &= -v_s(\mathbf{r}) && (98) \end{aligned}$$

where in the second line we used $\hat{H}_s\Phi_s = E_s\Phi_s$. So we obtain

$$\frac{\delta T_s}{\delta n(\mathbf{r})} = -v_s[n](\mathbf{r}) \tag{99}$$

Therefore the variational equation Eq.(95) becomes

$$v_s[n](\mathbf{r}) = v_0(\mathbf{r}) + v_{\mathrm{H}}[n](\mathbf{r}) + v_{\mathrm{xc}}[n](\mathbf{r}) \tag{100}$$

The functionals $v_s[n]$ is implicitly defined by the KS equations. Therefore combining this expression with the KS equations leads to a determining equation for the density that is equivalent to Eq.(80):

$$\begin{aligned}\big(-\frac{1}{2}\nabla^2 \;&+\; v_s[n](\mathbf{r})\big)\phi_i(\mathbf{r}\sigma) = \epsilon_i\phi_i(\mathbf{r}\sigma) &(101)\\ n(\mathbf{r}) \;&=\; \sum_\sigma\sum_{i=1}^N |\phi_i(\mathbf{r}\sigma)|^2 &(102)\\ v_s[n](\mathbf{r}) \;&=\; v_0(\mathbf{r}) + v_{\mathrm{H}}[n](\mathbf{r}) + v_{\mathrm{xc}}[n](\mathbf{r}) &(103)\\ v_{\mathrm{xc}}[n](\mathbf{r}) \;&=\; \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} &(104)\end{aligned}$$

So, given an approximation to $E_{\mathrm{xc}}[n]$ or $v_{\mathrm{xc}}[n](\mathbf{r})$ this set of equations can be solved to self-consistency, whihc then yields density n. If we insert this into the energy functional this then yields the total energy of the system. The main task that remains now is to find a good approximation for the xc-energy and the xc-potential.

B. The Hellman-Feynman theorem

The Hellman-Feynman theorem is a simple result regarding the derivative of the energy with respect to a parameter in the Hamiltonian. Let $\hat{H}_\lambda$ be a Hamiltonian depending on a parameter λ. Then by the solution of the Schrödinger equation also the ground state energy E_λ and the grounds state wave function Ψ_λ depend on λ, i.e.

$$\hat{H}_\lambda\Psi_\lambda = E_\lambda\Psi_\lambda \tag{105}$$

The energy can therefore also be written as

$$E_\lambda = \langle\Psi_\lambda|\hat{H}_\lambda|\Psi_\lambda\rangle \tag{106}$$

If we differentiate this expression with respect to λ and use that Ψ_λ is an eigenstate of the Hamiltonian $\hat{H}_\lambda$ then we obtain

$$\begin{aligned}\frac{dE_\lambda}{d\lambda} \;&=\; \frac{d}{d\lambda}\langle\Psi_\lambda|\hat{H}_\lambda|\Psi_\lambda\rangle = \langle\frac{d\Psi_\lambda}{d\lambda}|\hat{H}_\lambda|\Psi_\lambda\rangle + \langle\Psi_\lambda|\frac{d\hat{H}_\lambda}{d\lambda}|\Psi_\lambda\rangle + \langle\Psi_\lambda|\hat{H}_\lambda|\frac{d\Psi_\lambda}{d\lambda}\rangle\\ &=\; E_\lambda\Big(\langle\frac{d\Psi_\lambda}{d\lambda}|\Psi_\lambda\rangle + \langle\Psi_\lambda|\frac{d\Psi_\lambda}{d\lambda}\rangle\Big) + \langle\Psi_\lambda|\frac{d\hat{H}_\lambda}{d\lambda}|\Psi_\lambda\rangle\\ &=\; E_\lambda\frac{d}{d\lambda}\langle\Psi_\lambda|\Psi_\lambda\rangle + \langle\Psi_\lambda|\frac{d\hat{H}_\lambda}{d\lambda}|\Psi_\lambda\rangle = \langle\Psi_\lambda|\frac{d\hat{H}_\lambda}{d\lambda}|\Psi_\lambda\rangle \qquad (107)\end{aligned}$$

where we used that $\langle\Psi_\lambda|\Psi_\lambda\rangle = 1$ for all λ. So we thus obtain the simple result that

$$\frac{dE_\lambda}{d\lambda} = \langle\Psi_\lambda|\frac{d\hat{H}_\lambda}{d\lambda}|\Psi_\lambda\rangle \tag{108}$$

This is known as the Hellman-Feynman theorem. So if we need to know the change of the energy with respect to some parameter in the Hamiltonian then we only need to evaluate the expectation value of the of the derivative of the Hamiltonian with respect to this parameter.

C. The coupling constant integration

Now we are going to apply the Hellman-Feynman theorem to a special case which is very useful to give the exchange-correlation energy functional a physical interpretation. We consider a Hamiltonian of the form

$$\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda\hat{W} \tag{109}$$

In this Hamiltonian we multiplied the two-particle interaction with a parameter λ and consequently the ground state wave function Ψ_λ is also a a function of λ. The potential $\hat{V}_\lambda$ is now constructed in suc a way that for each value of λ the density remains the same, i.e. is independent of λ:

$$n(\mathbf{r}) = \langle \Psi_\lambda | \hat{n}(\mathbf{r}) | \Psi_\lambda \rangle \quad \forall \lambda \tag{110}$$

According to the Hohenberg-Kohn theorem such a potential $v_\lambda(\mathbf{r})$ is unique up to a constant. The endpoints $\lambda = 1$ and $\lambda = 0$ are special. At $\lambda = 1$ we take the interacting system that we are interested in

$$\hat{H}_{\lambda=1} = \hat{T} + \hat{V} + \hat{W} \tag{111}$$

where $\hat{V} = \hat{V}_{\lambda=1}$ is the potential for our system of interest and $\hat{W}$ is the Coulombi replusion between the electrons. At $\lambda = 0$ we have a noninteracting system with the same density as the interacting system, i.e. this is simply the Kohn-Sham system corresponding to the interacting system of interest:

$$\hat{H}_{\lambda=0} = \hat{V} + \hat{V}_s \tag{112}$$

where $\hat{V}_s = \hat{V}_{\lambda=0}$. let E_λ now be the ground state energy of the system a coupling strength λ, then from the Hellman-Feynman theorem we can write

$$\begin{aligned} E_{\lambda=1} - E_{\lambda=0} &= \int_0^1 d\lambda \frac{dE_\lambda}{d\lambda} = \int_0^1 d\lambda \, \langle \Psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \Psi_\lambda \rangle = \int_0^1 d\lambda \, \langle \Psi_\lambda | \frac{d\hat{V}_\lambda}{d\lambda} + \hat{W} | \Psi_\lambda \rangle \\ &= \int_0^1 d\lambda \int d^3\mathbf{r} \frac{dv_\lambda(\mathbf{r})}{d\lambda} n(\mathbf{r}) + \int_0^1 d\lambda \langle \Psi_\lambda | \hat{W} | \Psi_\lambda \rangle \\ &= \int d^3\mathbf{r} (v_{\lambda=1}(\mathbf{r}) - v_{\lambda=0}(\mathbf{r})) n(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \int_0^1 d\lambda \, \Gamma_\lambda(\mathbf{r}, \mathbf{r}') w(\mathbf{r}, \mathbf{r}') \\ &= \int d^3\mathbf{r} (v(\mathbf{r}) - v_s(\mathbf{r})) n(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \, \bar{\Gamma}(\mathbf{r}, \mathbf{r}') w(\mathbf{r}, \mathbf{r}') \end{aligned} \tag{113}$$

where we defined the coupling constant integrated diagonal density matrix as

$$\bar{\Gamma}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda \, \Gamma_\lambda(\mathbf{r}, \mathbf{r}') \tag{114}$$

In this expression Γ_λ is the diagonal two-particle density matrix for a system with coupling strenght λ and ground state density $n(\mathbf{r})$. Now on the other hand we know that

$$E_{\lambda=0} = \langle \Phi_s[n] | \hat{T} + \hat{V}_s | \Phi_s[n] \rangle = T_s[n] + \int d^3 \, n(\mathbf{r}) v_s(\mathbf{r}) \tag{115}$$

If we combine this expression with Eq.(113) and writing $E_{\lambda=1} = E_v[n]$ then we obtain the result

$$E_v[n] = T_s[n] + \int d^3\mathbf{r} \, n(\mathbf{r}) v(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \, \bar{\Gamma}(\mathbf{r}, \mathbf{r}') w(\mathbf{r}, \mathbf{r}') \tag{116}$$

On the other hand we already knew that from Eq.(94)

$$\begin{aligned} E_v[n] &= F_{\mathrm{HK}}[n] + \int d^3\mathbf{r} \, n(\mathbf{r}) v(\mathbf{r}) \\ &= T_s[n] + \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \, n(\mathbf{r}) n(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') + E_{\mathrm{xc}}[n] \end{aligned} \tag{117}$$

Combining the last two equations the gives the following result for the exchange-correlation energy functional

$$E_{\mathrm{xc}}[n] = \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}'\,[\bar{\Gamma}(\mathbf{r},\mathbf{r}') - n(\mathbf{r})n(\mathbf{r}')]w(\mathbf{r},\mathbf{r}') \tag{118}$$

The exchange-correlation energy functional can therefore directly be expressed in terms of a pair-correlation function. This expression has found to be very useful in the construction of approximate density functionals, as well will see later.

D. The exchange-correlation hole

In the following we will discuss a number of two-particle correlation functions that have played an important role in analyzing the properties of interacting many-body systems. An important quantity is the pair-correlation function $g(\mathbf{r},\mathbf{r}')$ defined as

$$g(\mathbf{r},\mathbf{r}') = \frac{\Gamma(\mathbf{r},\mathbf{r}')}{n(\mathbf{r})n(\mathbf{r}')} \tag{119}$$

This function describes how much the density marix Γ deviates from a simple product. In an infinite extended system, such as the electron gas the function g approaches 1 if $|\mathbf{r}-\mathbf{r}'| \to \infty$ and attains values between 0 and 1 for different values. If we want to use the pair-correlation function within density functional theory then we need to replace g by its coupling constant average $\bar{g}$ which is defined in terms of $\bar{\Gamma}$ as

$$\bar{g}(\mathbf{r},\mathbf{r}') = \frac{\bar{\Gamma}(\mathbf{r},\mathbf{r}')}{n(\mathbf{r})n(\mathbf{r}')} \tag{120}$$

If we insert this into Eq.(118) then the xc-energy attains the form

$$E_{\mathrm{xc}}[n] = \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}'\,n(\mathbf{r})n(\mathbf{r}')[\bar{g}(\mathbf{r},\mathbf{r}') - 1]w(\mathbf{r},\mathbf{r}') \tag{121}$$

Let us derive some useful property of $\bar{g}$. It is clear that the diagonal density matrix Γ_λ has the property (see Eq.(44))

$$(N-1)n(\mathbf{r}) = \int d^3\mathbf{r}'\,\Gamma_\lambda(\mathbf{r},\mathbf{r}') \tag{122}$$

Since the density is independent of λ (by construction) we can intergrate both sides over λ to obtain

$$(N-1)n(\mathbf{r}) = \int d^3\mathbf{r}'\,\bar{\Gamma}(\mathbf{r},\mathbf{r}') = n(\mathbf{r})\int d^3\mathbf{r}'\,n(\mathbf{r}')\bar{g}(\mathbf{r},\mathbf{r}') \tag{123}$$

We therefore see that

$$\int d^3\mathbf{r}'\,n(\mathbf{r}')\bar{g}(\mathbf{r},\mathbf{r}') = N-1 \tag{124}$$

and consequently since the density integrates to N we obtain the following sumrule for the pair-correlation function

$$\int d^3\mathbf{r}'\,n(\mathbf{r}')[\bar{g}(\mathbf{r},\mathbf{r}') - 1] = -1 \tag{125}$$

The quantity under the integral sign is often denoted as the coupling constant integrated exchange-correlation hole $\bar{n}_{\rm xc}$. This is a quantity that has a clear physical interpretation. We can write

$$\bar{n}_{\rm xc}(\mathbf{r}'|\mathbf{r}) = n(\mathbf{r}')[\bar{g}(\mathbf{r},\mathbf{r}') - 1] = \frac{\bar{\Gamma}(\mathbf{r},\mathbf{r}')}{n(\mathbf{r})} - n(\mathbf{r}') \tag{126}$$

The first term

$$\rho(\mathbf{r}'|\mathbf{r}) = \frac{\bar{\Gamma}(\mathbf{r},\mathbf{r}')}{n(\mathbf{r})} \tag{127}$$

describes the conditional probability density to find an electron at $\mathbf{r}'$ given the fact that there is an electron at $\mathbf{r}$. This probability density integrates to the remaining $N-1$ electrons since we already know that an electron was fixed at postion $\mathbf{r}$, i.e.

$$\int d^3\mathbf{r}'\rho(\mathbf{r}'|\mathbf{r}) = N - 1 \tag{128}$$

In the last term we subtract from $\rho(\mathbf{r}'|\mathbf{r})$ the unconditional density $n(\mathbf{r}')$ to find an electron at $\mathbf{r}'$,i.e.

$$\bar{n}_{\rm xc}(\mathbf{r}'|\mathbf{r}) = \rho(\mathbf{r}'|\mathbf{r}) - n(\mathbf{r}') \tag{129}$$

The difference between those integrates to minus one which is the charge of the reference electron missing from the charge cloud. This is the physical interpretation of the sumrule in Eq.(125). The exhange-correlation energy of Eq.(121) can therefore also be written as

$$E_{\rm xc}[n] = \frac{1}{2}\int d^3\mathbf{r} d^3\mathbf{r}' n(\mathbf{r})\bar{n}_{\rm xc}(\mathbf{r}'|\mathbf{r})w(\mathbf{r},\mathbf{r}') \tag{130}$$

with

$$\int d^3\mathbf{r}'\,\bar{n}_{\rm xc}(\mathbf{r}'|\mathbf{r}) = -1 \tag{131}$$

Therefore the xc-energy is complete determined by the xc-hole. In fact, it is completely determined by its spherical average. We can write

$$E_{\rm xc}[n] = \frac{1}{2}\int d^3\mathbf{r} n(\mathbf{r})\int d^3\mathbf{r}'\frac{\bar{n}_{\rm xc}(\mathbf{r}'|\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{2}\int d^3\mathbf{r} n(\mathbf{r})\int d^3\mathbf{u}\frac{\bar{n}_{\rm xc}(\mathbf{r}+\mathbf{u}|\mathbf{r})}{|\mathbf{u}|} \tag{132}$$

where we defined the difference vector $\mathbf{r}' = \mathbf{r}+\mathbf{u}$. Since the two-particle interaction depends only on the lenghth $|\mathbf{u}|$ of $\mathbf{u}$ we can write

$$E_{\rm xc}[n] = \frac{1}{2}\int d\mathbf{r}\, n(\mathbf{r})\int_0^\infty du\, 4\pi u \bar{n}_{\rm xc}(\mathbf{r},u) \tag{133}$$

where we defined the spherically averaged xc-hole by the relation

$$\bar{n}_{\rm xc}(\mathbf{r},u) = \frac{1}{4\pi}\int d\Omega_{\mathbf{u}}\,\bar{n}_{\rm xc}(\mathbf{r}+\mathbf{u}|\mathbf{r}) \tag{134}$$

where $d\Omega_{\mathbf{u}}$ denotes integration over the angular variables. The spherically averaged xc-hole is readily seen to have the sum rule property

$$\int_0^\infty du\, 4\pi u^2\,\bar{n}_{\rm xc}(\mathbf{r},u) = \int_0^\infty du\, u^2\int d\Omega_{\mathbf{u}}\,\bar{n}_{\rm xc}(\mathbf{r}+\mathbf{u}|\mathbf{r}) = -1 \tag{135}$$

E. Splitting into exchange and correlation

We can further split the exchange-correlation functional into two pieces, an exchange part and a correlation part. We can define the exchange energy by the expression

$$E_{\mathrm{x}}[n] = \langle \Phi_s[n] | \hat{W} | \Phi_s[n] \rangle - E_{\mathrm{H}}[n] \tag{136}$$

where $\Phi_s[n]$ is the Kohn-Sham determinant and E_{H} is the Hartree energy of Eq.(93). It is simply the expectation value of the two-particle energy using an independent particle wavefunction. It incorporates the anti-symmetry of the wave function (hence the name exchange)) but does not include correlations between particles of unlike spin. The remaining correlations are inlcude in the correlation functional

$$E_{\mathrm{c}}[n] = E_{\mathrm{xc}}[n] - E_{\mathrm{x}}[n] \tag{137}$$

such that we have a splitup $E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}$ of the exchange-correlation energy into an exchange and a correlation part. We can further define the exchange part of the pair-correlation function as

$$g_{\mathrm{x}}(\mathbf{r}, \mathbf{r}') = \frac{\langle \Phi_s[n] | \hat{\Gamma}(\mathbf{r}, \mathbf{r}') | \Phi_s[n] \rangle}{n(\mathbf{r}) n(\mathbf{r}')} \tag{138}$$

which is simply the pair-correlation function of a single Slater-determinant wave function. From the definition of the exchange energy we see that we have the expression

$$E_{\mathrm{x}}[n] = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \, n(\mathbf{r}) n(\mathbf{r}') [g_{\mathrm{x}}(\mathbf{r}, \mathbf{r}') - 1] w(\mathbf{r}, \mathbf{r}') \tag{139}$$

If we define the correlation part $\bar{g}_{\mathrm{c}}$ of the pair-correlation function to be

$$\bar{g}_{\mathrm{c}}(\mathbf{r}, \mathbf{r}') = \frac{\bar{\Gamma}(\mathbf{r}, \mathbf{r}') - \langle \Phi_s[n] | \hat{\Gamma}(\mathbf{r}, \mathbf{r}') | \Phi_s[n] \rangle}{n(\mathbf{r}) n(\mathbf{r}')} \tag{140}$$

(i.e. we split $\bar{g} = g_x + \bar{g}_{\mathrm{c}}$) then the correlation energy can be written as

$$E_{\mathrm{c}}[n] = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \, n(\mathbf{r}) n(\mathbf{r}') \bar{g}_{\mathrm{c}}(\mathbf{r}, \mathbf{r}') w(\mathbf{r}, \mathbf{r}') \tag{141}$$

We can further split the exchange-correlation hole into an exchange and a correlation part as $\bar{n}_{\mathrm{xc}} = n_{\mathrm{x}} + \bar{n}_{\mathrm{c}}$ if we define the exchange and correlation holes as

$$\begin{aligned} n_{\mathrm{x}}(\mathbf{r}'|\mathbf{r}) &= n(\mathbf{r}')(g_{\mathrm{x}}(\mathbf{r}, \mathbf{r}') - 1) & (142) \\ \bar{n}_{\mathrm{c}}(\mathbf{r}'|\mathbf{r}) &= n(\mathbf{r}') \bar{g}_{\mathrm{c}}(\mathbf{r}, \mathbf{r}') & (143) \end{aligned}$$

It is easliy checked that the exchange and correlation holes satisfy the properties

$$\begin{aligned} \int d^3\mathbf{r}' \, n_{\mathrm{x}}(\mathbf{r}'|\mathbf{r}) &= -1 & (144) \\ \int d^3\mathbf{r}' \, \bar{n}_{\mathrm{c}}(\mathbf{r}'|\mathbf{r}) &= 0 & (145) \end{aligned}$$

The functions g_{x} and n_{x} can be explicitly calculated in terms of the Kohn-Sham orbitals. We find

$$\begin{aligned} \langle \Phi_s[n] | \hat{\Gamma}(\mathbf{r}, \mathbf{r}') | \Phi_s[n] \rangle &= \sum_{\sigma\sigma'} \gamma_s(\mathbf{r}\sigma, \mathbf{r}\sigma) \gamma_s(\mathbf{r}'\sigma', \mathbf{r}'\sigma') - \gamma_s(\mathbf{r}\sigma, \mathbf{r}'\sigma') \gamma_s(\mathbf{r}'\sigma', \mathbf{r}\sigma) \\ &= n(\mathbf{r}) n(\mathbf{r}') - \sum_{\sigma\sigma'} |\gamma_s(\mathbf{r}\sigma, \mathbf{r}'\sigma')|^2 & (146) \end{aligned}$$

where

$$\gamma_s(\mathbf{r}\sigma, \mathbf{r}'\sigma') = \sum_i^N \phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}\sigma) \tag{147}$$

is the one-particle density matrix of the Kohn-Sham system. We therefore obtain the expression for the exchange part of the pair-correlation function

$$g_{\mathrm{x}}(\mathbf{r}, \mathbf{r}') = 1 - \sum_{\sigma\sigma'} \frac{|\gamma_s(\mathbf{r}\sigma, \mathbf{r}'\sigma')|^2}{n(\mathbf{r})n(\mathbf{r}')} \tag{148}$$

From Eq.(139) we then see that the exchange energy has the expression

$$E_{\mathrm{x}}[n] = -\frac{1}{2}\sum_{\sigma\sigma'} \int d^3\mathbf{r}d^3\mathbf{r}' \, \frac{|\gamma_s(\mathbf{r}\sigma, \mathbf{r}'\sigma')|^2}{|\mathbf{r}-\mathbf{r}'|} \tag{149}$$

If we consider the case of a spin-compensated system with orbitals as in Eq.(87) we can write the one-particle density matrix as

$$\gamma_s(\mathbf{r}\sigma, \mathbf{r}'\sigma') = (\delta_{\sigma,\uparrow}\delta_{\sigma',\uparrow} + \delta_{\sigma,\downarrow}\delta_{\sigma',\downarrow}) \sum_i^{N/2} \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}') = \delta_{\sigma\sigma'} \sum_i^{N/2} \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}') \tag{150}$$

We can therefore introduce a spin-integrated one-particle density matrix

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_\sigma \gamma_s(\mathbf{r}\sigma, \mathbf{r}'\sigma) = 2\sum_i^{N/2} \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}') \tag{151}$$

and therefore in terms of this density matrix the exchange energy attains the form

$$E_{\mathrm{x}}[n] = -\frac{1}{2}\sum_{\sigma\sigma'} \frac{\delta_{\sigma\sigma'}}{4} \int d^3\mathbf{r}d^3\mathbf{r}' \, \frac{|\gamma_s(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} = -\frac{1}{4}\int d^3\mathbf{r}d^3\mathbf{r}' \, \frac{|\gamma_s(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \tag{152}$$

Similarly for the exchange part g_{x} of the pair correlation function we obtain

$$g_{\mathbf{x}}(\mathbf{r}, \mathbf{r}') - 1 = -\sum_{\sigma\sigma'} \frac{\delta_{\sigma\sigma'}}{4} \frac{|\gamma_s(\mathbf{r}, \mathbf{r}')|^2}{n(\mathbf{r})n(\mathbf{r}')} = -\frac{1}{2}\frac{|\gamma_s(\mathbf{r}, \mathbf{r}')|^2}{n(\mathbf{r})n(\mathbf{r}')} \tag{153}$$

As an example we calculate g_{x} and n_{x} for the case of a spin compensated two-particle system described by the Kohn-Sham equations Eq.(85) and (86). In this case we have a single level uccupied by a an up and a down spin electron with the same spatial orbital. The Kohn-Sham equation is given by

$$\begin{aligned} \big(-\frac{1}{2}\nabla^2 \;&+\; v_s(\mathbf{r})\big)\varphi(\mathbf{r}) = \epsilon\varphi(\mathbf{r}) && (154)\\ n(\mathbf{r}) \;&=\; 2|\varphi(\mathbf{r})|^2 && (155) \end{aligned}$$

Then the spin-integrated one-particle density matrix is given by

$$\gamma_s(\mathbf{r}, \mathbf{r}') = 2\varphi^*(\mathbf{r})\varphi(\mathbf{r}) \tag{156}$$

We then obtain from Eq.(153) and (142) for the g_{x} and n_{x} the expressions

$$\begin{aligned} g_{\mathrm{x}}(\mathbf{r}, \mathbf{r}') \;&=\; \frac{1}{2} && (157)\\ n_{\mathrm{x}}(\mathbf{r}'|\mathbf{r}) \;&=\; \frac{1}{2}n(\mathbf{r}') && (158) \end{aligned}$$

V. CONSTRAINED SEARCH AND DOMAIN QUESTIONS

A. v-representability

The functional $F_{\mathrm{HK}}[n]$ is defined on the set of densities that are obtained from ground state wave functions of interacting systems with external potential v. Such densities are called interacting-v-representable densities. On the other hand, the functional $T_s[n]$ was defined for a ground state densities of noninteracting systems. Such densities are called noninteracting-v-representable. The Kohn-Sham construction is therefore only valid when every interacting-v-representable density is also noninteracting-v-representable. For the case of lattice systems this known to be true (see [4]). One can further prove that the set noninteracting-v-representable densities is dense (in Banach norm) in the set of interacting v-representable densities. This means that a Kohn-Sham scheme can be set up that yields a given interacting-v-representable density to arbitrary accuracy. Further exact results for the continuum case are not known.

B. Domain extensions

The domains of the functionals $T_s[n]$ and $F_{\mathrm{HK}}[n]$ can be extended by means of the constrained search construction. We can write for the ground state energy

$$E_0 = \underset{\Psi}{\mathrm{Min}} \langle \Psi | \hat{H} | \Psi \rangle = \underset{n}{\mathrm{Min}} \left(\underset{\Psi \to n}{\mathrm{Min}} \langle \Psi | \hat{H} | \Psi \rangle \right) = \underset{n}{\mathrm{Min}}\, E_{\mathrm{LL},v}[n] \tag{159}$$

where we defined the Levy-Lieb functional $E_{\mathrm{LL},v}[n]$ by

$$E_{\mathrm{LL},v}[n] = \underset{\Psi \to n}{\mathrm{Min}} \langle \Psi | \hat{H} | \Psi \rangle \tag{160}$$

in which we minimize the energy for all wavefunctions Ψ that yield density n. The Levy-Lieb functional can be written as

$$E_{\mathrm{LL},v}[n] = F_{\mathrm{LL}}[n] + \int d^3\, n(\mathbf{r}) v(\mathbf{r}) \tag{161}$$

where we defined

$$F_{\mathrm{LL}}[n] = \underset{\Psi \to n}{\mathrm{Min}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \tag{162}$$

So in this case we minimize over all wave functions for which

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \tag{163}$$

and we do not care if Ψ is the ground state of some Hamiltonian. We only require Ψ to be anti-symmetric and normalized such that the densities integrate to N particles. The set of densities that come from normalized anti-symmetric wave functions are called N-representable. One can show that any continuous density that satisfies $n(\mathbf{r}) \geq 0$ and that integrates to N particles is N-representable. This set is larger than the set of v-representable densities. The functional $F_{\mathrm{LL}}[n]$ is an extension of the functional $H_{\mathrm{HK}}[n]$ in the sense that

$$F_{\mathrm{LL}}[n] = F_{\mathrm{HK}}[n] \tag{164}$$

whenever n is v-representable. This follows immediately because

$$\begin{aligned} F_{\mathrm{HK}}[n] + \int d^3\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) &= \langle \Psi[n] | \hat{T} + \hat{V} + \hat{W} | \Psi[n] \rangle = \underset{\Psi \to n}{\mathrm{Min}} \langle \Psi | \hat{T} + \hat{V} + \hat{W} | \Psi \rangle \\ &= F_{\mathrm{LL}}[n] + \int d^3\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) \end{aligned} \tag{165}$$

Since we have

$$E_0 \leq F_{\rm LL}[n] + \int d^3\mathbf{r}\, n(\mathbf{r}) v(\mathbf{r}) \tag{166}$$

we need to minimize over the N-representable densities to obtain the ground state density n_0. This leads to the variation equation

$$\frac{\delta F_{\rm LL}[n]}{\delta n(\mathbf{r})} = -v(\mathbf{r}) \tag{167}$$

However, using this derivative there is an important point to take into account. One can show that the functional derivative of $F_{\rm LL}$ only exists for the v-representable densities. This means that for the study of the variational equations of density functional theory we anyway have to consider the question of v-representability.

In the remainder of these notes we will not go into the domain questions anymore and instead focus on the construction of approximate density functionals.

VI. THE LOCAL DENSITY APPROXIMATION

A. The homogeneous electron gas

We will now study a system that has been used as the basis of many density functional approximations. The system consists of a box of N interacting electrons. The volume of the box is given by $V = L^3$ where L is the lenght of the box. Eventually we will take the limit $L \to \infty$ while keeping the number of electrons per volume unit N/V constant. The system will then have (apart from boundary effects) a constant density given by $n = N/V$. The electrons in the box repel each other by the Coulomb repulsion. Therefore the system is only stable if we add a homogeneous postive background charge. If we think of this as a simple model of a solid we may imagine that the positive nuclei are smeared out into a 'jelly'. This model is therefore also known as the jellium model.

B. The Kohn-System for the homogeneous electron gas

The Kohn-Sham system representing the homogeneous electron gas is rather simple. It consists of noninteracting electrons in a box with density $n = N/V$ where we take the limit $L \to \infty$ while keeping the density the same. Since the density is constant also the Kohn-Sham potential $v_s(n)$ will be a constant and therefore we can simply put $v_s = 0$ such that the Kohn-Sham equations only contain the kinetic energy operator. We thus have

$$-\frac{1}{2}\nabla^2 \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \tag{168}$$

If we use periodic boundary conditions $\phi_i(x+L,y,z) = \phi_i(x,y,z)$ (and similar in the other two directions) for the orbitals then they have the form

$$\psi_{\mathbf{k}}(\mathbf{r}\sigma) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \chi(\sigma) \tag{169}$$

where $\chi(\sigma)$ is a spin function and we defined the $\mathbf{k}$-vector

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_2) \tag{170}$$

with n_i integers. The Kohn-Sham eigenvalues are simply given by $\epsilon_{\mathbf{k}} = |\mathbf{k}|^2/2$ as one can check immediately by inserting the form of the orbitals (169) into the Kohn-Sham equations (168). We consider a spin-compendated case in which we occupy all levels up to a certain levels ϵ_{F} (which we will call the Fermi level) with one up spin and one down spin electron. We therefore have to consider all **k**-vectors such that

$$\frac{1}{2}|\mathbf{k}|^2 \leq \epsilon_{\mathrm{F}} \tag{171}$$

This represents a sphere in momentum space, also known as the Fermi sphere. We further define a Fermi wave vector by the equation

$$k_{\mathrm{F}}^2 = 2\epsilon_{\mathrm{F}} \tag{172}$$

Then the number of electrons in the system is given by the equation

$$N = 2 \sum_{|\mathbf{k}| \leq k_{\mathrm{F}}} \sum 1 = 2 \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_{\mathrm{F}}} d^3\mathbf{k} = \frac{2V}{(2\pi)^3} \frac{4}{3} \pi k_{\mathrm{F}}^3 \tag{173}$$

Here we used that

$$\sum_{n_1,n_2,n_3} \simeq \int dn_1 dn_2 dn_3 = \frac{V}{(2\pi)^3} \int d^3\mathbf{k} \tag{174}$$

which is valid if have have many states in the Fermi sphere (i.e. for $L \to \infty$). From Eq.(173) we see that

$$k_{\mathrm{F}}^3 = 3\pi^2 \frac{N}{V} \tag{175}$$

or equivalently

$$k_{\mathrm{F}} = (3\pi^2\, n)^{1/3} \tag{176}$$

We can now calculated the kinetic energy of the Kohn-Sham system (which is also the total energy). We have

$$\begin{aligned} T_s[n] &= 2 \sum_{|\mathbf{k}| \leq k_{\mathrm{F}}} \epsilon_{\mathbf{k}} = \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_{\mathrm{F}}} d^3\mathbf{k}\, |\mathbf{k}|^2 = \frac{V}{(2\pi)^3}\, 4\pi \int_0^{k_{\mathrm{F}}} dk\, k^4 = \frac{V}{2\pi^2} \frac{1}{5} k_{\mathrm{F}}^5 \\ &= \frac{V}{10} \frac{(3\pi^2)^{5/3}}{\pi^2}\, n^{5/3} = V\, \frac{3}{10} (3\pi^2)^{2/3}\, n^{5/3} \end{aligned} \tag{177}$$

The kinetic energy per volume unit is therefore given by

$$\frac{T[n]}{V} = \frac{3}{10} (3\pi^2)^{2/3}\, n^{5/3} \tag{178}$$

If we then would consider a weakly inhomogeneous system then we may argue that we could locally at point **r**regard the system as a homogeneous electron gas with energy density of Eq. (178). In that case we have

$$T_s[n] = \frac{3}{10} (3\pi^2)^{2/3} \int d^3\mathbf{r}\, n(\mathbf{r})^{5/3} \tag{179}$$

This is the Thomas-Fermi approximation for the kinetic energy. The approximation is not very good for very inhomogeneous systems as atoms, molecules and solids. It does, among other things, not reproduce the proper electronic shell structure of atomic densities. However, since $T_s[n]$ is treated exactly within the Kohn-Sham scheme we can try a similar approximation for the exchange-correlation energy. Let us calculate the exchange energy first. We start by evaluating the one-particle density matrix. If we define $u = |\mathbf{r} - \mathbf{r}'|$ and $t = K_{\mathrm{F}} u$ then we can write

$$\begin{aligned}
\gamma_s(\mathbf{r},\mathbf{r}') &= 2 \sum_{|\mathbf{k}|\leq k_{\mathrm{F}}} \frac{1}{V}\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \frac{2}{(2\pi)^3} \int_{|\mathbf{k}|\leq k_{\mathrm{F}}} d^3\mathbf{k}\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \\
&= \frac{1}{4\pi^3}\, 2\pi \int_0^{k_{\mathrm{F}}} dk\, k^2 \int_0^{\pi} d\theta\, \sin\theta\, e^{iku\cos\theta} \\
&= \frac{1}{2\pi^2} \int_0^{k_{\mathrm{F}}} dk\, k^2 \big[-\frac{1}{iku} e^{iku\cos\theta} \big]_0^{\pi} \\
&= \frac{1}{2\pi^2} \int_0^{k_{\mathrm{F}}} dk\, k^2 \big(\frac{e^{iku} - e^{-iku}}{iku} \big) = \frac{1}{\pi^2 u} \int_0^{k_{\mathrm{F}}} dk\, k\, \sin(ku) \\
&= -\frac{1}{\pi^2 u}\frac{\partial}{\partial u} \int_0^{k_{\mathrm{F}}} dk\, \cos(ku) = -\frac{1}{\pi^2 u}\frac{\partial}{\partial u} \big(\frac{\sin k_F u}{u} \big) \\
&= \frac{k_{\mathrm{F}}^3}{\pi^2}\, \frac{\sin t - t\cos t}{t^3} = 3n\, \frac{\sin t - t\cos t}{t^3} \qquad (180)
\end{aligned}$$

We therefore obtain for $g_{\mathbf{x}}(\mathbf{r},\mathbf{r}')$ the expression

$$g_{\mathbf{x}}(\mathbf{r},\mathbf{r}') - 1 = -\frac{1}{2} \frac{|\gamma_s(\mathbf{r},\mathbf{r}')|^2}{n(\mathbf{r}) n(\mathbf{r}')} = -\frac{9}{2} \big(\frac{\sin t - t\cos t}{t^3} \big)^2 \qquad (181)$$

Summarizing

$$g_{\mathbf{x}}(\mathbf{r},\mathbf{r}') = 1 - \frac{9}{2} \big(\frac{\sin t - t\cos t}{t^3} \big)^2 \qquad t = k_{\mathrm{F}} |\mathbf{r} - \mathbf{r}'| \qquad (182)$$

having obtained the pair-correlation function we can further calculate the exchange energy density:

$$\begin{aligned}
\epsilon_{\mathbf{x}} &= \frac{1}{2} \int d^3\mathbf{r}'\, \frac{n_{\mathrm{x}}(\mathbf{r}'|\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \\
&= \frac{1}{2} \int d^3\mathbf{r}' \frac{n}{|\mathbf{r}-\mathbf{r}'|} (g_{\mathrm{x}}(\mathbf{r},\mathbf{r}') - 1) = -\frac{9n}{4} \int d^3\mathbf{u}\, \frac{1}{u} \big(\frac{\sin k_{\mathrm{F}} u - k_{\mathrm{F}} u \cos k_{\mathrm{F}} u}{(k_{\mathrm{F}} u)^3} \big)^2 \\
&= -9n\pi \int_0^{\infty} du\, u\, \big(\frac{\sin k_{\mathrm{F}} u - k_{\mathrm{F}} u \cos k_{\mathrm{F}} u}{(k_{\mathrm{F}} u)^3} \big)^2 = -\frac{9\pi n}{k_{\mathrm{F}}^2} \int_0^{\infty} dt\, \frac{(\sin t - t\cos t)^2}{t^5} \\
&= -\frac{9\pi n}{4 k_{\mathrm{F}}^2} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{1/3} \qquad (183)
\end{aligned}$$

Here we used that

$$\int_0^{\infty} dt\, \frac{(\sin t - t\cos t)^2}{t^5} = \frac{1}{4} \qquad (184)$$

The exchange energy is then given by

$$E_{\mathrm{x}} = \int d^3\mathbf{r}\, n \epsilon_x = -V \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{4/3} \qquad (185)$$

Then the energy density per volume unit is given by

$$\varepsilon_{\mathrm{x}} = \frac{E_{\mathrm{x}}}{V} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3} \tag{186}$$

If we now make the local density approximation for a weakly inhomogeneous system, then

$$E_{\mathrm{x}}^{\mathrm{LDA}}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d^3\mathbf{r}\, n(\mathbf{r})^{4/3} \tag{187}$$

The same expression is obtained if for the exchange-hole we use the expression

$$n_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r}'|\mathbf{r}) = n(\mathbf{r})(g_{\mathbf{x}}(k_{\mathrm{F}}(\mathbf{r})|\mathbf{r}-\mathbf{r}'|) - 1) \tag{188}$$

where $k_{\mathrm{F}} = (3\pi^2 n(\mathbf{r}))^{1/3}$. This follows immediately form the fact that the derivation of Eq.(183) would go through if we would have give the density a spatial dependence on the coordinate $\mathbf{r}$. Let us check that the exchange-hole properly integrates to -1. We have that

$$\begin{aligned}
\int d^3\mathbf{r}'\, n_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r}'|\mathbf{r}) &= n(\mathbf{r}) \int d^3\mathbf{r}'\, (g_{\mathrm{x}}(k_{\mathrm{F}}(\mathbf{r})|\mathbf{r}-\mathbf{r}'|) - 1) \\
&= -\frac{9n(\mathbf{r})}{2} \int d^3\mathbf{r}'\, \big(\frac{\sin t - t\cos t}{t^3}\big)^2 \\
&= -18\pi n(\mathbf{r}) \int_0^\infty du\, u^2\, \big(\frac{\sin t - t\cos t}{t^3}\big)^2 \\
&= -\frac{18\pi n(\mathbf{r})}{k_{\mathrm{F}}^3(\mathbf{r})} \int_0^\infty dt\, \big(\frac{\sin t - t\cos t}{t^2}\big)^2 \\
&= -\frac{18\pi n(\mathbf{r})}{3\pi^2 n(\mathbf{r})} \frac{\pi}{6} = -1
\end{aligned} \tag{189}$$

where we used that

$$\int_0^\infty dt\, \big(\frac{\sin t - t\cos t}{t^2}\big)^2 = \frac{\pi}{6} \tag{190}$$

It is now clear that we can apply the local density approximation to the correlation energy as well. Then we have

$$E_{\mathrm{c}}^{\mathrm{LDA}}[n] = \int d^3\mathbf{r}\, \varepsilon_{\mathrm{c}}(n(\mathbf{r})) \tag{191}$$

where $\varepsilon_{\mathrm{c}}(n)$ is the correlation energy per volume unit of the homogeneous electron gas. The corresponding approximation for the correlation hole is

$$\bar{n}_{\mathrm{c}}^{\mathrm{LDA}}(\mathbf{r}'|\mathbf{r}) = n(\mathbf{r})\bar{g}_{\mathrm{c}}(n(\mathbf{r}), |\mathbf{r}-\mathbf{r}'|) \tag{192}$$

where $\bar{g}_{\mathrm{c}}$ is the coupling constant integrated pair-correlation function of the homogeneous electron gas [5]. So in total the LDA expression for the exchange-correlation energy becomes

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int d^3\mathbf{r}\, \varepsilon_{\mathrm{xc}}(n(\mathbf{r})) \tag{193}$$

where $\varepsilon_{\mathrm{xc}}(n) = \varepsilon_{\mathrm{x}}(n) + \varepsilon_{\mathrm{c}}(n)$ is the exchange-correlation energy per volume unit of the homogeneous electron gas. The corresponding xc-potential is given by

$$v_{\mathrm{xc}}^{\mathrm{LDA}}[n](\mathbf{r}) = \frac{d\varepsilon_{\mathrm{xc}}}{dn}\Big|_{n=n(\mathbf{r})} = -\left(\frac{3}{\pi}\right)^{1/3} n(\mathbf{r})^{1/3} \tag{194}$$

In a finite system, like an atom or molecule, this densitydecays exponentially since the density decays exponentially. This is a violation of the exact condition $v_{\mathrm{x}} \sim -1/|\mathbf{r}|$ for $|\mathbf{r}| \to \infty$ (we will come to this point later).
In view of the assumptions made in the derivation one may think that the LDA does not work well in systems with strong density variations, as is present in atoms and molecules. However, for these systems the approximation works much better than one would expect. For an extensive discussion of the performance of the LDA we refer to the review paper by von Barth [1]. An explanation for the success of the LDA can be given from a comparison of the exact and LDA hole functions [3]. In this paper it is shown that the LDA and exact hole functions are not very close but that their spherical averages are close. As we have seen the xc-energy is completely determined by these spherical averages.

VII. THE STRAIGHTFORWARD GRADIENT EXPANSION

A. The functional Taylor expansion of the xc-energy

In this section we will show how to systematically derive corrections to the LDA. In fact the LDA will appear naturally from our theory. We consider a general density profile $n(\mathbf{r}) = n_0 + \delta n(\mathbf{r})$ where n_0 is a constant density and where

$$\int d^3\mathbf{r}\, \delta n(\mathbf{r}) = 0 \tag{195}$$

so we consider a density modulation around a fixed background density n_0. Later we will assume that $\delta n(\mathbf{r})$ is slowly varying such that an expansion in density derivatives is possible. However, for the moment we can keep $\delta n(\mathbf{r})$ to be rather general. The xc-energy functional can then be expanded around n_0 using the following functional Taylor expansion

$$E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}[n_0] + \sum_{m=1}^{\infty} \frac{1}{m!} \int d^{3m}\mathbf{r}\, K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 \ldots \mathbf{r}_m) \delta n(\mathbf{r}_1) \ldots \delta n(\mathbf{r}_m) \tag{196}$$

where we defined

$$d^{3m}\mathbf{r} = d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_m \tag{197}$$

and

$$K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 \ldots \mathbf{r}_m) = \frac{\delta^m E_{\mathrm{xc}}}{\delta n(\mathbf{r}_1) \ldots \delta n(\mathbf{r}_m)}\Big|_{n=n_0} \tag{198}$$

Since the homogeneous electron gas is invariant under translations, rotations and inversion, the functions $K_{\mathrm{xc}}^{(m)}$ (which are evaluated at a constant density n_0) satisfy the following symmetry properties:

$$\begin{aligned} K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 \ldots \mathbf{r}_m) &= K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 + \mathbf{a} \ldots \mathbf{r}_m + \mathbf{a}) && (199) \\ K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 \ldots \mathbf{r}_m) &= K_{\mathrm{xc}}^{(m)}(n_0; R\mathbf{r}_1 \ldots R\mathbf{r}_m) && (200) \\ K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 \ldots \mathbf{r}_m) &= K_{\mathrm{xc}}^{(m)}(n_0; -\mathbf{r}_1, \ldots, -\mathbf{r}_m) && (201) \end{aligned}$$

for all tranlation vectors $\mathbf{a}$ and all rotation matrices R. Moreover, because of the definition of the response functions they are invariant under permutations, i.e.

$$K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_1 \ldots \mathbf{r}_m) = K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{r}_{\pi(1)} \ldots \mathbf{r}_{\pi(m)}) \tag{202}$$

for all permutations π of the numbers $(1,\ldots,m)$. From translational invariance property of Eq.(199) we see by taking $\mathbf{a}=-\mathbf{r}_1$ that

$$K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\ldots\mathbf{r}_m)=K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{0},\mathbf{r}_2-\mathbf{r}_1,\ldots,\mathbf{r}_m-\mathbf{r}_1) \tag{203}$$

and therefore $K_{\mathrm{xc}}^{(m)}$ only depends on $m-1$ difference vectors. We therefore define the functions

$$L^{(m)}(n_0;\mathbf{r}_2-\mathbf{r}_1,\ldots,\mathbf{r}_m-\mathbf{r}_1)=K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{r}_1\ldots\mathbf{r}_m) \tag{204}$$

of $m-1$ variables. Let us give a few examples for the functions $K_{\mathrm{xc}}^{(m)}$ and $L^{(m)}$:

$$\begin{aligned}
K_{\mathrm{xc}}^{(1)}(n_0;\mathbf{r}_1) &= \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r}_1)}\Big|_{n=n_0}=v_{\mathrm{xc}}(n_0)=\text{Constant} && (205)\\
K_{\mathrm{xc}}^{(2)}(n_0;\mathbf{r}_1,\mathbf{r}_2) &= \frac{\delta^2 E_{\mathrm{xc}}}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\Big|_{n=n_0}=L^{(2)}(n_0;\mathbf{r}_2-\mathbf{r}_1) && (206)
\end{aligned}$$

If we insert these terms in the expansion Eq.(196) we have

$$\begin{aligned}
E_{\mathrm{xc}}[n] &= E_{\mathrm{xc}}[n_0]+\int d^3\, v_{\mathrm{xc}}(n_0)\delta n(\mathbf{r})\\
&+ \frac{1}{2}\int d^3\mathbf{r}_1\int d^3\mathbf{r}_1\, L^{(2)}(n_0;\mathbf{r}_2-\mathbf{r}_1)\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)+\ldots\\
&= E_{\mathrm{xc}}[n_0]+\frac{1}{2}\int d^3\mathbf{r}_1\int d^3\mathbf{r}_1\, L^{(2)}(n_0;\mathbf{r}_2-\mathbf{r}_1)\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)+\ldots && (207)
\end{aligned}$$

where the term which is first order in $\delta n(\mathbf{r})$ disappears due to the condition of Eq.(195). The strategy that we are going to follow to obtain the gradient expansion is to expand the functions $K_{\mathrm{xc}}^{(m)}$ into Fourier vectors which when transformed back to real space leads to an expansion in density gradients. This procedure will become more clear when we proceed. We first define the Fourier transform of an m-point function and its inverse as as

$$\begin{aligned}
f(\mathbf{q}_1\ldots\mathbf{q}_m) &= \int d^{3m}\mathbf{r}\, f(\mathbf{r}_1\ldots\mathbf{r}_m)e^{-i\mathbf{q}_1\cdot\mathbf{r}_1-\ldots-i\mathbf{q}_m\cdot\mathbf{r}_m} && (208)\\
f(\mathbf{r}_1\ldots\mathbf{r}_m) &= \int \frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\, f(\mathbf{q}_1\ldots\mathbf{q}_m)e^{i\mathbf{q}_1\cdot\mathbf{r}_1+\ldots+i\mathbf{q}_m\cdot\mathbf{r}_m} && (209)
\end{aligned}$$

Using Eq.(209) we can now write the functional Taylor expansion of Eq.(196) in Fourier space as

$$\begin{aligned}
&E_{\mathrm{xc}}[n]=E_{\mathrm{xc}}[n_0]\\
&+\sum_{m=1}^{\infty}\frac{1}{m!}\int d^{3m}\mathbf{r}\int\frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\,K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m)e^{i\mathbf{q}_1\cdot\mathbf{r}_1+\ldots+i\mathbf{q}_m\cdot\mathbf{r}_m}\delta n(\mathbf{r}_1)\ldots\delta n(\mathbf{r}_m)\\
&= E_{\mathrm{xc}}[n_0]+\sum_{m=1}^{\infty}\frac{1}{m!}\int\frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\,K_{\mathrm{xc}}^{(m)}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m)\delta n(-\mathbf{q}_1)\ldots\delta n(-\mathbf{q}_m) && (210)
\end{aligned}$$

We now can express the Fourier transform of $K_{\rm xc}^{(m)}$ in terms of the functions $L^{(m)}$. The Fourier transform of $K_{\rm xc}^{(m)}$ is given by

$$
\begin{aligned}
K_{\rm xc}^{(m)}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m) &= \int d^{3m}\mathbf{r}\, K_{\rm xc}^{(m)}(n_0;\mathbf{r}_1\ldots\mathbf{r}_m)e^{-i\mathbf{q}_1\cdot\mathbf{r}_1-\ldots-i\mathbf{q}_m\cdot\mathbf{r}_m} \\
&= \int d^{3m}\mathbf{r}\, L^{(m)}(n_0;\mathbf{r}_2-\mathbf{r}_1\ldots\mathbf{r}_m-\mathbf{r}_1)e^{-i\mathbf{q}_1\cdot\mathbf{r}_1-\ldots-i\mathbf{q}_m\cdot\mathbf{r}_m} \\
&= \int d^3\mathbf{r}_1\int d^3\mathbf{r}'_2\ldots\int d^3\mathbf{r}'_m\, L^{(m)}(n_0;\mathbf{r}'_2\ldots\mathbf{r}'_m)e^{-i\mathbf{q}_1\cdot\mathbf{r}'_2-\ldots-i\mathbf{q}_m\cdot\mathbf{r}'_m}e^{-i(\mathbf{q}_1+\ldots+\mathbf{q}_m)\cdot\mathbf{r}_1} \\
&= (2\pi)^3\,\delta(\mathbf{q}_1+\ldots+\mathbf{q}_m)\,L^{(m)}(n_0;\mathbf{q}_2\ldots\mathbf{q}_m)
\end{aligned} \tag{211}
$$

where in the third line of this equation we used the substitution $\mathbf{r}'_i=\mathbf{r}_i-\mathbf{r}_1\,(i=2\ldots m)$ and we further used the identity

$$
\int d^3\mathbf{r}\, e^{-i\mathbf{q}\cdot\mathbf{r}} = (2\pi)^3\,\delta(\mathbf{q}) \tag{212}
$$

If we further insert the expression of Eq.(211) into the Taylor expansion Eq.(210), and remember from Eq.(207) that the term with $m=1$ does not contribute, then we obtain the expansion

$$
\begin{aligned}
&E_{\rm xc}[n] = E_{\rm xc}[n_0] \\
&+\sum_{m=2}^{\infty}\frac{1}{m!}\int\frac{d^3\mathbf{q}_2}{(2\pi)^3}\ldots\frac{d^3\mathbf{q}_m}{(2\pi)^3}L^{(m)}(n_0;\mathbf{q}_2\ldots\mathbf{q}_m)\delta n(\mathbf{q}_2+\ldots+\mathbf{q}_m)\delta(-\mathbf{q}_2)\ldots\delta n(-\mathbf{q}_m)
\end{aligned} \tag{213}
$$

This is the Taylor expansion that we will use to derive the gradient expansion. The first terms from Eq.(213) are given by

$$
\begin{aligned}
E_{\rm xc}[n] &= E_{\rm xc}[n_0]+\frac{1}{2}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\,L^{(2)}(n_0;\mathbf{q})\delta n(\mathbf{q})\delta n(-\mathbf{q}) \\
&+ \frac{1}{6}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\frac{d^3\mathbf{q}'}{(2\pi)^3}\,L^{(3)}(n_0;\mathbf{q},\mathbf{q}')\delta n(\mathbf{q}+\mathbf{q}')\delta n(-\mathbf{q})\delta n(-\mathbf{q}')+\ldots\ldots
\end{aligned} \tag{214}
$$

The gradient expansion is derived by expanding the functions $L^{(m)}$ into powers of the vectors $\mathbf{q}_i$ and then Fourier transforming back to real space.

B. A consistency condition

Before we continue to discuss the expansion of the functions $L^{(m)}$ we first discuss a consistency condition that is crucial for the existence of the gradient expansion [6]. It follows from the definition of the functions $K_{\rm xc}^{(m)}$ that

$$
\delta K_{\rm xc}^{(m)}(n_0;\mathbf{r}_1\ldots\mathbf{r}_m) = \int d^3\mathbf{r}\,K_{\rm xc}^{(m+1)}(n_0;\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_m)\delta n(\mathbf{r}) \tag{215}
$$

If we now take $\delta(\mathbf{r})=\delta_0=$ Constant, then we obtain the condition

$$
\frac{\partial K_{\rm xc}^{(m)}}{\partial n_0}(n_0;\mathbf{r}_1\ldots\mathbf{r}_m) = \int d^3\mathbf{r}\,K_{\rm xc}^{(m+1)}(n_0;\mathbf{r},\mathbf{r}_1\ldots\mathbf{r}_m) \tag{216}
$$

We have, for example, using Eq.(205)

$$\begin{aligned}\frac{\partial v_{\mathrm{xc}}}{\partial n_0} &= \frac{K^{(1)}_{\mathrm{xc}}}{\partial n_0} = \int d^3\mathbf{r}_1\, K^{(2)}_{\mathrm{xc}}(n_0;\mathbf{r}_1,\mathbf{r}_2) = \int d^3\mathbf{r}_1\, L^{(2)}(n_0;\mathbf{r}_2-\mathbf{r}_1) \\ &= \int d^3\mathbf{r}' L^{(2)}(n_0;\mathbf{r}') = L^{(2)}(n_0;\mathbf{q}=0) \end{aligned} \tag{217}$$

This property is quite general: the zero **q**-limit of the functions $L^{(m+1)}$ can be determined from the a derivative of the function $L^{(m)}$ with respect to n_0. Let us present the derivation. We first write condition Eq.(216) in terms of the functions $L^{(m)}$. From the definition of $L^{(m)}$ of Eq.(204) we see immediately that

$$\frac{\partial L^{(m)}}{\partial n_0}(n_0;\mathbf{r}_2-\mathbf{r}_1\ldots\mathbf{r}_m-\mathbf{r}_1) = \int d^3\mathbf{r}\, L^{(m+1)}(n_0;\mathbf{r}_1-\mathbf{r}\ldots\mathbf{r}_m-\mathbf{r}) \tag{218}$$

If we write both sides of this equation in terms of their Fourier transforms we find

$$\begin{aligned}&\int \frac{d^3\mathbf{q}_2}{(2\pi)^3}\cdots\frac{d^3\mathbf{q}_m}{(2\pi)^3}\,\frac{\partial L^{(m)}}{\partial n_0}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m)e^{i\mathbf{q}_2\cdot(\mathbf{r}_2-\mathbf{r}_1)+\ldots+i\mathbf{q}_m\cdot(\mathbf{r}_m-\mathbf{r}_1)} \\ &= \int d^3\mathbf{r}\int\frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\,L^{(m+1)}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m)e^{i\mathbf{q}_1\cdot(\mathbf{r}_1-\mathbf{r})+\ldots+i\mathbf{q}_m\cdot(\mathbf{r}_m-\mathbf{r})} \\ &= \int\frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\,(2\pi)^3\delta(\mathbf{q}_1+\ldots+\mathbf{q}_m)\,L^{(m+1)}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m)e^{i\mathbf{q}_1\cdot\mathbf{r}_1+\ldots+i\mathbf{q}_m\cdot\mathbf{r}_m} \\ &= \int\frac{d^3\mathbf{q}_2}{(2\pi)^3}\cdots\frac{d^3\mathbf{q}_m}{(2\pi)^3}\,L^{(m+1)}(n_0;-\mathbf{q}_2\ldots-\mathbf{q}_m,\mathbf{q}_2\ldots\mathbf{q}_m)e^{i\mathbf{q}_2\cdot(\mathbf{r}_2-\mathbf{r}_1)+\ldots+i\mathbf{q}_m\cdot(\mathbf{r}_m-\mathbf{r}_1)}\end{aligned}$$

where in the last step we used $\mathbf{q}_1 = -\mathbf{q}_2\ldots-\mathbf{q}_m$. By comparing the Fourier components on both sides of this equation we obtain the result

$$\frac{\partial L^{(m)}}{\partial n_0}(n_0;\mathbf{q}_2\ldots\mathbf{q}_m) = L^{(m+1)}(n_0;-\mathbf{q}_2\ldots-\mathbf{q}_m,\mathbf{q}_2\ldots\mathbf{q}_m) \tag{219}$$

This is an important relation that we will use to eliminate the n_0-dependence in the gradient expansion.

C. Polynomial structure of the response functions

We are now ready for the discussion of the expansion of the functions $K^{(m)}_{\mathrm{xc}}$ and $L^{(m)}$ in terms of **q**-vectors. If we assume that a Taylor-expansion in powers of $\mathbf{q}_i$ exists We can write

$$\begin{aligned}&K^{(m)}_{\mathrm{xc}}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m) = (2\pi)^3\delta(\mathbf{q}_1+\ldots+\mathbf{q}_m) \\ &\quad\times\ \left[K^{(m)}_0(n_0)+K^{(m)}_1(n_0)P^{(m)}_1(\mathbf{q}_1\ldots\mathbf{q}_m)+K^{(m)}_2(n_0)P^{(m)}_2(\mathbf{q}_1\ldots\mathbf{q}_m)+\ldots\right]\end{aligned} \tag{220}$$

where $P^{(m)}_i$ are polynomials in $\mathbf{q}_1\ldots\mathbf{q}_m$ and $K^{(m)}_i(n_0)$ coefficients depending on n_0. It follows directly from Eqs.(200) and (201) that the function $K^{(m)}_{\mathrm{xc}}$ satisfies the relations (check for yourself!)

$$K^{(m)}_{\mathrm{xc}}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m) = K^{(m)}_{\mathrm{xc}}(n_0;R\mathbf{q}_1\ldots R\mathbf{q}_m) \tag{221}$$

$$K^{(m)}_{\mathrm{xc}}(n_0;\mathbf{q}_1\ldots\mathbf{q}_m) = K^{(m)}_{\mathrm{xc}}(n_0;-\mathbf{q}_1\ldots-\mathbf{q}_m) \tag{222}$$

for any rotation matrix R. The main question to answer therefore is:

- What polynomials in $\mathbf{q}_1 \ldots \mathbf{q}_m$ are invariant under rotations and inversions?

This is a purely mathematical question, that relates to group theory. The answer can be found in the classic book by H.Weyl [7]. The answer is:

- Every polynomial that is invariant under rotations and inversions can be expressed as a polynomials in the variables $Q_{ij} = \mathbf{q}_i \cdot \mathbf{q}_j$.

If we had not insisted on inversion then (in three dimensions, or general odd dimensions) there would be another odd invariant, namely the determinant $|\mathbf{q}_i \mathbf{q}_j \mathbf{q}_k|$ of any three vectors $\mathbf{q}_i$. The product of such determinants would give an even invariant but this is readily seen to be a polynomial in Q_{ij} as well and does not give new invariants [7]. It is clear that the variables Q_{ij} themselves are invariant under rotations and inversions

$$\begin{aligned} Q_{ij} &= \mathbf{q}_i \cdot \mathbf{q}_j = (R\mathbf{q}_i) \cdot (R\mathbf{q}_j) && (223) \\ Q_{ij} &= \mathbf{q}_i \cdot \mathbf{q}_j = (-\mathbf{q}_i) \cdot (-\mathbf{q}_j) && (224) \end{aligned}$$

so every polynomial in these variables is invariant as well. The functions $K_{\rm xc}^{(m)}$ also exhibit permutational symmetry

$$K_{\rm xc}^{(m)}(n_0; \mathbf{q}_1 \ldots \mathbf{q}_m) = K_{\rm xc}^{(m)}(n_0; \mathbf{q}_{\pi(1)} \ldots \mathbf{q}_{\pi(m)}) \tag{225}$$

for any permutaion π of the numbers $1 \ldots m$ and therefore we only need to consider symmetric polynomials (this fact also excludes polynomial invariants that contain terms linear in determinants of $\mathbf{q}$-vectors are these terms are anti-symmetric rather than symmetric). So we conclude that the polynomials $P_i^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m)$ of Eq.(220) are symmetric polynomials in the variables $Q_{ij} = \mathbf{q}_i \cdot \mathbf{q}_j$. Let us give a few examples. The lowest order polynomials (apart from a trivial constant) are the symmetric polynomials that are linear in Q_{ij}. There are just two of them

$$\begin{aligned} P_1^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) &= \sum_{i=1}^{m} Q_{ii} = \mathbf{q}_1^2 + \ldots + \mathbf{q}_m^2 && (226) \\ P_2^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) &= \sum_{i>j}^{m} Q_{ij} = \mathbf{q}_2 \cdot \mathbf{q}_1 + \mathbf{q}_3 \cdot \mathbf{q}_2 + \mathbf{q}_3 \cdot \mathbf{q}_1 + \ldots && (227) \end{aligned}$$

To second order in Q_{ij} there are more possibilities:

$$\begin{aligned} P_3^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) &= \sum_{i}^{m} Q_{ii}^2 && (228) \\ P_4^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) &= \sum_{i>j}^{m} Q_{ii} Q_{jj} && (229) \\ P_5^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) &= \sum_{i,k>l}^{m} Q_{ii} Q_{kl} && (230) \\ P_6^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) &= \sum_{i>j,\, k>l}^{m} Q_{ij} Q_{kl} && (231) \\ P_7^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) &= \sum_{i>j}^{m} Q_{ij}^2 && (232) \end{aligned}$$

However, since in the expansion for $K_{\mathrm{xc}}^{(m)}$ we have the additional condition that $\mathbf{q}_1 + \ldots + \mathbf{q}_m = 0$ these polynomials are not independent. For instance from

$$\begin{aligned} 0 = (\mathbf{q}_1 + \ldots + \mathbf{q}_m)^2 &= \sum_i^m \mathbf{q}_i^2 + 2 \sum_{i>j}^m \mathbf{q}_i \cdot \mathbf{q}_j \\ &= P_1^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) + 2 P_2^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) \end{aligned} \tag{233}$$

we find $P_2^{(m)} = -P_1^{(m)}/2$. It then also immediatley follows that $P_5^{(m)}$ and $P_6^{(m)}$ can be expressed in $P_3^{(m)}$ and $P_4^{(m)}$. By taking another square of Eq.(233) we then see that also $P_7^{(m)}$ can be expressed in $P_3^{(m)}$ and $P_4^{(m)}$. For this reason the expansion of Eq.(220) can be written as

$$\begin{aligned} &K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{q}_1 \ldots \mathbf{q}_m) = (2\pi)^3 \delta(\mathbf{q}_1 + \ldots + \mathbf{q}_m) \\ &\quad \times \ \left[L_0^{(m)}(n_0) + L_1^{(m)}(n_0) \Pi_1^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) + L_2^{(m)}(n_0) \Pi_2^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) + \ldots \right] \end{aligned} \tag{234}$$

where relabeled $K_0^{(m)} = L_0^{(m)}$ and where the first three lowest order polynomials have the form

$$\Pi_1^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) = \sum_i^m Q_{ii} \tag{235}$$

$$\Pi_2^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) = \sum_i^m Q_{ii}^2 \tag{236}$$

$$\Pi_3^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) = \sum_{i>j}^m Q_{ii} Q_{jj} \tag{237}$$

From the relation Eq.(211)

$$K_{\mathrm{xc}}^{(m)}(n_0; \mathbf{q}_1 \ldots \mathbf{q}_m) = (2\pi)^3 \delta(\mathbf{q}_1 + \ldots + \mathbf{q}_m) L^{(m)}(n_0; \mathbf{q}_2 \ldots \mathbf{q}_m) \tag{238}$$

Therefore the function $L^{(m)}$ has the expansion

$$\begin{aligned} L^{(m)}(n_0; \mathbf{q}_2 \ldots \mathbf{q}_m) &= L_0^{(m)}(n_0) + L_1^{(m)}(n_0) \pi_1^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) \\ &\quad + L_2^{(m)}(n_0) \pi_2^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) + \ldots \end{aligned} \tag{239}$$

where we defined the polynomials

$$\pi_j^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) = \Pi_j^{(m)}(-\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) \tag{240}$$

From Eq.(235) we see that the polynomial $\pi_1^{(m)}$ has the explicit form

$$\begin{aligned} \pi_1^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) &= (-\mathbf{q}_2 - \ldots - \mathbf{q}_m)^2 + \mathbf{q}_2^2 + \ldots + \mathbf{q}_m^2 \\ &= 2(\mathbf{q}_2^2 + \ldots + \mathbf{q}_m^2) + 2 \sum_{i>j\geq 2}^m \mathbf{q}_i \cdot \mathbf{q}_j \end{aligned} \tag{241}$$

Now we are going to derive a relation between the coefficients $L_j^{(m)}(n_0)$ and $L_j^{(m+1)}(n_0)$. To do this we use the consistency relation (219). If we insert Eq.(239) into Eq.(219) then on the lefthand side of this equation we have

$$\begin{aligned} \frac{\partial L^{(m)}}{\partial n_0}(n_0; \mathbf{q}_2 \ldots \mathbf{q}_m) &= \frac{\partial L_0^{(m)}}{\partial n_0}(n_0) + \frac{\partial L_1^{(m)}}{\partial n_0}(n_0) \pi_1^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) \\ &\quad + \frac{\partial L_2^{(m)}}{\partial n_0}(n_0) \pi_2^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) + \ldots \end{aligned} \tag{242}$$

whereas on the righthand side we have

$$\begin{aligned}
&L^{(m+1)}(n_0; -\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) \\
&= L_0^{(m+1)}(n_0) + L_1^{(m+1)}(n_0)\pi_1^{(m+1)}(-\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) \\
&\quad + L_2^{(m+1)}(n_0)\pi_2^{(m+1)}(-\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) + \ldots \qquad (243)
\end{aligned}$$

Let us look more closely at the polynomials in Eq.(243). From Eq.(241) we see that

$$\begin{aligned}
\pi_1^{(m+1)}(-\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) &= (-(-\mathbf{q}_2 - \ldots - \mathbf{q}_m) - \mathbf{q}_2 - \ldots - \mathbf{q}_m)^2 \\
&\quad + (-\mathbf{q}_2 - \ldots - \mathbf{q}_m)^2 + \mathbf{q}_2^2 + \ldots + \mathbf{q}_m^2 \\
&= \pi_1^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) \qquad (244)
\end{aligned}$$

This is not a coincidence. The polynomials in Eqs.(235)-(237) have the property that

$$\Pi_j^{(m+1)}(0, \mathbf{q}_1 \ldots \mathbf{q}_m) = \Pi_j^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) \qquad (245)$$

but then it follows from the definition of $\pi_j^{(m)}$ of Eq.(240) that

$$\begin{aligned}
\pi_j^{(m+1)}(-\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) &= \Pi_j^{(m+1)}(0, -\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) \\
&= \Pi_j^{(m)}(-\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) \\
&= \pi_j^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) \qquad (246)
\end{aligned}$$

Therefore the expansion of Eq.(243) attains the form

$$\begin{aligned}
L^{(m+1)}(n_0; -\mathbf{q}_2 - \ldots - \mathbf{q}_m, \mathbf{q}_2 \ldots \mathbf{q}_m) &= L_0^{(m+1)}(n_0) + L_1^{(m+1)}(n_0)\pi_1^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) \\
&\quad + L_2^{(m+1)}(n_0)\pi_2^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) + \ldots \qquad (247)
\end{aligned}$$

If we compare this equation to the Eq.(242) we see that we obtain the following relations between the coefficients

$$L_j^{(m+1)}(n_0) = \frac{\partial L_j^{(m)}}{\partial n_0}(n_0) \qquad (248)$$

These are the key equations that will allow us to construct the gradient expansion. If we compare Eq.(217) to the expansion (239) we see that

$$L_0^{(2)}(n_0) = \frac{\partial v_{\mathrm{xc}}}{\partial n_0} = \frac{\partial^2 \epsilon_{\mathrm{xc}}}{\partial n_0^2}(n_0) \qquad (249)$$

From the relations Eq.(248) we then see that

$$L_0^{(3)}(n_0) = \frac{\partial L_0^{(2)}}{\partial n_0}(n_0) = \frac{\partial^3 \epsilon_{\mathrm{xc}}}{\partial n_0^3}(n_0) \qquad (250)$$

and subsequent use of Eq.(248)) leads to the general result

$$L_0^{(m)}(n_0) = \frac{\partial^m \epsilon_{\mathrm{xc}}}{\partial n_0^m}(n_0) \qquad (251)$$

Similarly we find that

$$L_1^{(3)}(n_0) = \frac{\partial L_1^{(2)}}{\partial n_0}(n_0) \qquad (252)$$

and in general

$$L_1^{(m)}(n_0) = \frac{\partial^{m-2} L_1^{(2)}}{\partial n_0^{m-2}}(n_0) \tag{253}$$

We are now ready to discuss the gradient expansion.

D. The gradient expansion

After all the preliminary work the gradient expansion is derived relatively easily. We insert the expansion of the function $L^{(m)}$ of eq.(239) in Eq.(213). This yields

$$\begin{aligned} E_{\mathrm{xc}}[n] &= E_{\mathrm{xc}}[n_0] \\ &+ \sum_{m=2}^{\infty} \frac{1}{m!} \int \frac{d^3\mathbf{q}_2}{(2\pi)^3} \ldots \frac{d^3\mathbf{q}_m}{(2\pi)^3} (L_0^{(m)}(n_0) + L_1^{(m)}(n_0)\pi_1^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) \\ &\quad + L_2^{(m)}(n_0)\pi_2^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m) + \ldots)\delta n(\mathbf{q}_2 + \ldots + \mathbf{q}_m)\delta(-\mathbf{q}_2) \ldots \delta n(-\mathbf{q}_m) \\ &= E_{\mathrm{xc}}[n_0] + \sum_{m=2}^{\infty} \frac{1}{m!} (L_0^{(m)}(n_0) A_0^{(m)} + L_1^{(m)}(n_0) A_1^{(m)} + L_2^{(m)}(n_0) A_2^{(m)} + \ldots) \end{aligned} \tag{254}$$

where we defined

$$A_0^{(m)} = \int \frac{d^3\mathbf{q}_2}{(2\pi)^3} \ldots \frac{d^3\mathbf{q}_m}{(2\pi)^3} \delta n(\mathbf{q}_2 + \ldots + \mathbf{q}_m)\delta(-\mathbf{q}_2) \ldots \delta n(-\mathbf{q}_m) \tag{255}$$

and

$$A_j^{(m)} = \int \frac{d^3\mathbf{q}_2}{(2\pi)^3} \ldots \frac{d^3\mathbf{q}_m}{(2\pi)^3}\ \pi_j^{(m)}(\mathbf{q}_2 \ldots \mathbf{q}_m)\delta n(\mathbf{q}_2 + \ldots + \mathbf{q}_m)\delta(-\mathbf{q}_2) \ldots \delta n(-\mathbf{q}_m) \tag{256}$$

for $j = 1, 2, \ldots$. The coefficient $A_0^{(m)}$ is readily calculated to be

$$\begin{aligned} A_0^{(m)} &= \int \frac{d^3\mathbf{q}_2}{(2\pi)^3} \ldots \frac{d^3\mathbf{q}_m}{(2\pi)^3} \int d^{3m}\mathbf{r}\, \delta n(\mathbf{r}_1) e^{i(\mathbf{q}_2 + \ldots \mathbf{q}_m)\dot{\mathbf{r}}_1} \delta n(\mathbf{r}_2) e^{-i\mathbf{q}_2 \cdot \mathbf{r}_2} \ldots \delta n(\mathbf{r}_m) e^{-i\mathbf{q}_m \cdot \mathbf{r}_m} \\ &= \int d^{3m}\mathbf{r}\, \delta(\mathbf{r}_1 - \mathbf{r}_2) \ldots \delta(\mathbf{r}_1 - \mathbf{r}_m) \delta n(\mathbf{r}_1) \ldots \delta n(\mathbf{r}_m) \\ &= \int d^3\mathbf{r}_1 (\delta n(\mathbf{r}_1))^m \end{aligned} \tag{257}$$

With this expression the first part of the expansion of Eq.(254) becomes

$$E_{\mathrm{xc}}[n_0] + \sum_{m=2}^{\infty} \frac{1}{m!} L_0^{(m)}(n_0) A_0^{(m)} = E_{\mathrm{xc}}[n_0] + \sum_{m=2}^{\infty} \frac{1}{m!} L_0^{(m)}(n_0) \int d^3\mathbf{r} (\delta n(\mathbf{r}))^m \tag{258}$$

If we now further use the explicit form of $L_0^{(m)}(n_0)$ from Eq.(251) as well as the equations

$$E_{\mathrm{xc}}[n_0] = \int d^3\mathbf{r}\, \epsilon_{\mathrm{xc}}(n_0) \tag{259}$$

$$0 = \int d^3\mathbf{r}\, \frac{\partial \epsilon_{\mathrm{xc}}}{\partial n_0}(n_0)\, \delta n(\mathbf{r}) \tag{260}$$

then we see that

$$\begin{aligned} E_{\rm xc}[n_0] + \sum_{m=2}^{\infty} \frac{1}{m!} L_0^{(m)}(n_0) A_0^{(m)} &= \int d^3\mathbf{r}\, \epsilon_{\rm xc}(n_0) + \sum_{m=1}^{\infty} \frac{1}{m!} \frac{\partial^m \epsilon_{\rm xc}}{\partial n_0^m}(n_0) \int d^3\mathbf{r} (\delta n(\mathbf{r}))^m \\ &= \int d^3\mathbf{r}\, \epsilon_{\rm xc}(n_0 + \delta n(\mathbf{r})) = \int d^3\mathbf{r}\, \epsilon_{\rm xc}(n(\mathbf{r})) \\ &= E_{\rm xc}^{\rm LDA}[n] \end{aligned} \tag{261}$$

So we have recovered the LDA from an infinite summation over response functions! Note that in this way we also have got rid of the explicit appearance of n_0. Now the general expansion for the exchange-correlation energy of Eq.(254) can be written as

$$E_{\rm xc}[n] = E_{\rm xc}^{\rm LDA}[n] + \sum_{m=2}^{\infty} \frac{1}{m!} (L_1^{(m)}(n_0) A_1^{(m)} + L_2^{(m)}(n_0) A_2^{(m)} + \ldots) \tag{262}$$

The remaining terms lead to gradient corrections to the LDA. To evaluate these corrections we have to study the coefficients $A_j^{(m)}$ for $j > 0$. To do this it the following idensity is useful

$$\int \frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}} (2\pi)^3 \delta(\mathbf{q}_1 + \ldots \mathbf{q}_m) f_1(-\mathbf{q}_1) \ldots f_m(-\mathbf{q}_m) = \int d^3\mathbf{r}\, f_1(\mathbf{r}) \ldots f_m(\mathbf{r}) \tag{263}$$

This is shown in exactly the same way as in the calculation of $A_0^{(m)}$, In fact, the special case $f_i(-\mathbf{q}_i) = \delta n(-\mathbf{q}_i)$ yields the earlier result for $A_0^{(m)}$ With this equation it is now relatively straightforward to calculate the coefficients $A_j^{(m)}$. since they are of the form

$$A_j^{(m)} = \int \frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}} (2\pi)^3 \delta(\mathbf{q}_1 + \ldots \mathbf{q}_m) \Pi_j^{(m)}(\mathbf{q}_1 \ldots \mathbf{q}_m) \delta n(-\mathbf{q}_1) \ldots \delta n(-\mathbf{q}_m) \tag{264}$$

where we used Eq.(256) and the definition Eq.(240) The polynomials $\Pi_1^{(m)}$, $\Pi_2^{(m)}$ and $\Pi_3^{(m)}$ are given in Eqs.(235)-(237). Inserting these into Eq.(264) yields the expressions

$$A_1^{(m)} = m \int \frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}} (2\pi)^3 \delta(\mathbf{q}_1 + \ldots \mathbf{q}_m)\, Q_{11} \delta n(-\mathbf{q}_1) \ldots \delta n(-\mathbf{q}_m) \tag{265}$$

$$A_2^{(m)} = m \int \frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}} (2\pi)^3 \delta(\mathbf{q}_1 + \ldots \mathbf{q}_m)\, Q_{11}^2 \delta n(-\mathbf{q}_1) \ldots \delta n(-\mathbf{q}_m) \tag{266}$$

$$A_3^{(m)} = \frac{1}{2} m(m-1) \int \frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}} (2\pi)^3 \delta(\mathbf{q}_1 + \ldots \mathbf{q}_m)\, Q_{11} Q_{22} \delta n(-\mathbf{q}_1) \ldots \delta n(-\mathbf{q}_m) \tag{267}$$

where we used that the integrands are symmetric functions. Now

$$Q_{ii} \delta n(-\mathbf{q}_i) = \mathbf{q}_i^2 \int d^3\mathbf{r}\, e^{i\mathbf{q}_i \cdot \mathbf{r}} \delta n(\mathbf{r}) = -\int d^3\mathbf{r}\, e^{i\mathbf{q}_i \cdot \mathbf{r}} \nabla^2 \delta n(\mathbf{r}) = f(-\mathbf{q}_i) \tag{268}$$

$$Q_{ii}^2 \delta n(-\mathbf{q}_i) = (\mathbf{q}_i^2)^2 \int d^3\mathbf{r}\, e^{i\mathbf{q}_i \cdot \mathbf{r}} \delta n(\mathbf{r}) = \int d^3\mathbf{r}\, e^{i\mathbf{q}_i \cdot \mathbf{r}} \nabla^2 (\nabla^2 \delta n(\mathbf{r})) = g(-\mathbf{q}_i) \tag{269}$$

with $f(\mathbf{r}) = -\nabla^2 \delta n(\mathbf{r})$ and $g(\mathbf{r}) = \nabla^2(\nabla^2 \delta n(\mathbf{r}))$. Then identity Eq.(263) tells us that

$$A_1^{(m)} = -m \int d^3\mathbf{r}\, (\nabla^2 \delta n(\mathbf{r}))\, \delta n(\mathbf{r})^{m-1} \tag{270}$$

$$A_2^{(m)} = m \int d^3\mathbf{r}\, \nabla^2 (\nabla^2 \delta n(\mathbf{r}))\, \delta n(\mathbf{r})^{m-1} \tag{271}$$

$$A_3^{(m)} = \frac{1}{2} m(m-1) \int d^3\mathbf{r}\, (\nabla^2 \delta n(\mathbf{r}))^2\, \delta n(\mathbf{r})^{m-2} \tag{272}$$

By partial integration the coefficients A_1^m and $A_2^{(m)}$ can be rewritten as

$$\begin{aligned} A_1^{(m)} &= m(m-1)\int d^3\mathbf{r}\,(\nabla\delta n(\mathbf{r}))^2\,\delta n(\mathbf{r})^{m-2} \qquad (273)\\ A_2^{(m)} &= -m(m-1)\int d^3\mathbf{r}\,\nabla(\nabla^2\delta n(\mathbf{r}))\cdot(\nabla\delta n(\mathbf{r}))\,\delta n(\mathbf{r})^{m-2}\\ &= m(m-1)\int d^3\mathbf{r}\,(\nabla^2\delta n(\mathbf{r}))^2\,\delta n(\mathbf{r})^{m-2}\\ &\quad +m(m-1)(m-2)\int d^3\mathbf{r}\,(\nabla^2\delta n(\mathbf{r}))(\nabla\delta n(\mathbf{r}))^2\,\delta n(\mathbf{r})^{m-3} \qquad (274)\end{aligned}$$

If we now insert Eqs.(272),(273) and (274) into the expansion of Eq.(262) we obtain the expansion

$$\begin{aligned} E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}^{\mathrm{LDA}}[n] &+ \sum_{m=2}^{\infty}\frac{1}{(m-2)!}L_1^{(m)}(n_0)\int d^3\mathbf{r}\,(\nabla\delta n(\mathbf{r}))^2\,\delta n(\mathbf{r})^{m-2}\\ &+ \sum_{m=2}^{\infty}\frac{1}{(m-2)!}L_2^{(m)}(n_0)\int d^3\mathbf{r}\,(\nabla^2\delta n(\mathbf{r}))^2\,\delta n(\mathbf{r})^{m-2}\\ &+ \sum_{m=3}^{\infty}\frac{1}{(m-3)!}L_2^{(m)}(n_0)\int d^3\mathbf{r}\,(\nabla^2\delta n(\mathbf{r}))(\nabla\delta n(\mathbf{r}))^2\,\delta n(\mathbf{r})^{m-3}\\ &+ \frac{1}{2}\sum_{m=2}^{\infty}\frac{1}{(m-2)!}L_3^{(m)}(n_0)\int d^3\mathbf{r}\,(\nabla^2\delta n(\mathbf{r}))^2\,\delta n(\mathbf{r})^{m-2}+\ldots \qquad (275)\end{aligned}$$

where the summation in the third line starts from $m=3$ since the second term in Eq.(274) is zero for $m=2$. Now from the relations Eq.(248) we deduce that

$$\begin{aligned} L_1^{(m)}(n_0) &= \frac{\partial^{m-2}L_1^{(2)}}{\partial n_0^{m-2}}(n_0) \qquad (276)\\ L_2^{(m)}(n_0) &= \frac{\partial^{m-2}L_2^{(2)}}{\partial n_0^{m-2}}(n_0) \qquad (277)\\ L_2^{(m)}(n_0) &= \frac{\partial^{m-3}L_2^{(3)}}{\partial n_0^{m-3}}(n_0) \qquad (278)\\ L_3^{(m)}(n_0) &= \frac{\partial^{m-2}L_3^{(2)}}{\partial n_0^{m-2}}(n_0) \qquad (279)\end{aligned}$$

If we further use that $\nabla n(\mathbf{r}) = \nabla(n_0+\delta n(\mathbf{r})) = \nabla\delta n(\mathbf{r})$ and relabel the summation indices then expansion Eq.(275) becomes:

$$\begin{aligned} E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}^{\mathrm{LDA}}[n] &+ \sum_{l=0}^{\infty}\frac{1}{l!}\frac{\partial^l L_1^{(2)}}{\partial n_0^l}(n_0)\int d^3\mathbf{r}\,(\nabla n(\mathbf{r}))^2\,\delta n(\mathbf{r})^l\\ &+ \sum_{l=0}^{\infty}\frac{1}{l!}\frac{\partial^l L_2^{(2)}}{\partial n_0^l}(n_0)\int d^3\mathbf{r}\,(\nabla^2 n(\mathbf{r}))^2\,\delta n(\mathbf{r})^l\\ &+ \sum_{l=0}^{\infty}\frac{1}{l!}\frac{\partial^l L_2^{(3)}}{\partial n_0^l}(n_0)\int d^3\mathbf{r}\,(\nabla^2 n(\mathbf{r}))(\nabla n(\mathbf{r}))^2\,\delta n(\mathbf{r})^l\\ &+ \frac{1}{2}\sum_{l=0}^{\infty}\frac{1}{l!}\frac{\partial^l L_3^{(2)}}{\partial n_0^l}(n_0)\int d^3\mathbf{r}\,(\nabla^2 n(\mathbf{r}))^2\,\delta n(\mathbf{r})^l+\ldots \qquad (280)\end{aligned}$$

Now we see that all the summations simply represent the Taylor expansions of the coefficients around n_0. We can therefore write

$$\begin{aligned}E_{\mathrm{xc}}[n] &= E_{\mathrm{xc}}^{\mathrm{LDA}}[n] + \int d^3\mathbf{r}\,(L_1^{(2)}(n_0+\delta n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 \\ &+ \int d^3\mathbf{r}\,(L_2^{(2)}(n_0+\delta n(\mathbf{r})) + \frac{1}{2}L_2^{(3)}(n_0+\delta n(\mathbf{r})))(\nabla^2 n(\mathbf{r}))^2 \\ &+ \int d^3\mathbf{r}\,L_2^{(3)}(n_0+\delta n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 + \dots \end{aligned} \tag{281}$$

So we finally obtain

$$\begin{aligned}E_{\mathrm{xc}}[n] &= E_{\mathrm{xc}}^{\mathrm{LDA}}[n] + \int d^3\mathbf{r}\,L_1^{(2)}(n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 \\ &+ \int d^3\mathbf{r}\,(L_2^{(2)}(n(\mathbf{r})) + \frac{1}{2}L_2^{(3)}(n(\mathbf{r})))(\nabla^2 n(\mathbf{r}))^2 \\ &+ \int d^3\mathbf{r}\,L_2^{(3)}(n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 + \dots \end{aligned} \tag{282}$$

These are the first terms in a systematic gradient expansion of the exchange-correlation energy. We see that we managed to eliminate the n_0-dependence by a complete summation over all response functions $L^{(m)}$ of order m. The first few coefficients are determined by a $\mathbf{q}$-expansion of the response functions $L^{(2)}$ and $L^{(3)}$ to fourth order in the $\mathbf{q}$-vectors. Let us look at these functions in more detail. We have according to Eq.(234)

$$\begin{aligned}K_{\mathrm{xc}}^{(2)}(n_0;\mathbf{q}_1,\mathbf{q}_2) &= (2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2)\big[L_0^{(2)}(n_0) + L_1^{(2)}(n_0)(Q_{11}+Q_{22}) \\ &\quad + L_2^{(2)}(n_0)(Q_{11}^2+Q_{22}^2) + L_3^{(2)}(n_0)Q_{11}Q_{22} + \dots\big] \\ &= (2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2)L^{(2)}(n_0;\mathbf{q}_2)\end{aligned} \tag{283}$$

where according to the deltafunction $Q_{11} = Q_{22}$. We thus find using $Q_{22} = |\mathbf{q}_2|^2$ that

$$L^{(2)}(n_0;\mathbf{q}_2) = L_0^{(2)}(n_0) + 2L_1^{(2)}(n_0)\,|\mathbf{q}_2|^2 + 2(L_2^{(2)}(n_0) + \frac{1}{2}L_3^{(2)}(n_0))|\mathbf{q}_2|^4 + \tag{284}$$

From this expression we see that the coefficients of the terms $(\nabla n)^2$ and $(\nabla^2 n)^2$ in the gradient expansion (282) correspond to twice the coefficients of $|\mathbf{q}|^2$ and $|\mathbf{q}|^4$ of the function $L^{(2)}(n_0;\mathbf{q})$. To obtain the coefficent $L_2^{(3)}$ that appears as coefficient of $(\nabla^2 n)(\nabla n)^2$ we need to consider the function $K_{\mathrm{xc}}^{(3)}$. This function has according to Eq.(234) the form

$$\begin{aligned}&K_{\mathrm{xc}}^{(3)}(n_0;\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = (2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\big[L_0^{(3)}(n_0) + L_1^{(2)}(n_0)(Q_{11}+Q_{22}+Q_{33}) \\ &\quad + L_2^{(3)}(n_0)(Q_{11}^2+Q_{22}^2+Q_{33}^2) + L_3^{(3)}(n_0)(Q_{11}Q_{22}+Q_{11}Q_{33}+Q_{22}Q_{33})\dots\big] \\ &= (2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)L^{(3)}(n_0;\mathbf{q}_2,\mathbf{q}_3)\end{aligned} \tag{285}$$

To determine $L^{(3)}(n_0;\mathbf{q}_2,\mathbf{q}_3)$ we have to eliminate $\mathbf{q}_1$ using $Q_{11} = \mathbf{q}_1^2 = (\mathbf{q}_2+\mathbf{q}_3)^2$. We then have, for instance

$$Q_{11}+Q_{22}+Q_{33} = (\mathbf{q}_2+\mathbf{q}_3)^2 + \mathbf{q}_2^2 + \mathbf{q}_3^2 = 2(\mathbf{q}_2^2+\mathbf{q}_3^2+\mathbf{q}_2\cdot\mathbf{q}_3) \tag{286}$$

The other terms can be calculated similarly. We find the expression

$$\begin{aligned}L^{(3)}(n_0;\mathbf{q}_2,\mathbf{q}_3) &= L_0^{(3)}(n_0) + 2L_1^{(3)}(n_0)(\mathbf{q}_2^2+\mathbf{q}_3^2+\mathbf{q}_2\cdot\mathbf{q}_3) \\ &+ (L_3^{(3)}(n_0) + 2L_2^{(3)}(n_0))(\mathbf{q}_2^2+\mathbf{q}_3^2+\mathbf{q}_2\cdot\mathbf{q}_3)^2 \\ &+ (L_3^{(3)}(n_0) - 2L_2^{(3)}(n_0))(\mathbf{q}_2^2\mathbf{q}_3^2 - (\mathbf{q}_2\cdot\mathbf{q}_3)^2) + \dots\end{aligned} \tag{287}$$

We therefore see that we can obtain $L_2^{(3)}(n_0)$ from the terms that are fourth order in the $\mathbf{q}$-vectors.

E. Example: The gradient expansion for exchange

Let us now give some explicit results for some of the gradient coefficients of the exchange functional. For the functional $E_{\mathrm{x}}[n]$ the function $L_{\mathrm{x}}^{(2)}$ (we subindex $L^{(2)}(n_0;\mathbf{q})$ with an x for clarity) has the expansion:

$$L_{\mathrm{x}}^{(2)}(n_0;\mathbf{q}) = -\frac{\pi}{k_{\mathrm{F}}^2}\big[1 + \frac{5}{36}\left(\frac{q}{k_{\mathrm{F}}}\right)^2 + \frac{73}{3600}\left(\frac{q}{k_{\mathrm{F}}}\right)^4 + \dots\big] \tag{288}$$

(we will discuss the calculation of this function later). This gives immediately the coefficients

$$\begin{aligned} 2L_1^{(2)}(n_0) &= -\frac{5\pi}{36k_{\mathrm{F}}^4} = -\frac{5}{108\pi}\frac{1}{(3\pi^2)^{1/3}}\frac{1}{n_0^{4/3}} && (289)\\ 2(L_2^{(2)}(n_0) + \frac{1}{2}L_3^{(2)}(n_0)) &= -\frac{73\pi}{3600k_{\mathrm{F}}^6} = -\frac{73}{32400\pi^3}\frac{1}{n_0^2} && (290)\end{aligned}$$

From Eq.(219) we then find then using $\partial k_{\mathrm{F}}/\partial n_0 = \pi^2/k_{\mathrm{F}}^2$ that

$$L_{\mathrm{x}}^{(3)}(n_0;-\mathbf{q},\mathbf{q}) = \frac{\partial L_{\mathrm{x}}^{(2)}}{\partial n_0}(n_0;\mathbf{q}) = \frac{2\pi^3}{k_{\mathrm{F}}^5}\big[1 + \frac{5}{18}\left(\frac{q}{k_{\mathrm{F}}}\right)^2 + \frac{73}{1200}\left(\frac{q}{k_{\mathrm{F}}}\right)^4 + \dots\big] \tag{291}$$

Therefore from Eq.(287)

$$\begin{aligned} L_{\mathrm{x}}^{(3)}(n_0;\mathbf{q}_2,\mathbf{q}_3) &= \frac{2\pi^3}{k_{\mathrm{F}}^5}\big[1 + \frac{5}{18}\frac{1}{k_{\mathrm{F}}^2}(\mathbf{q}_2^2 + \mathbf{q}_3^2 + \mathbf{q}_2\cdot\mathbf{q}_3)\\ &\quad + \frac{73}{1200}\frac{1}{k_{\mathrm{F}}^4}(\mathbf{q}_2^2 + \mathbf{q}_3^2 + \mathbf{q}_2\cdot\mathbf{q}_3)^2\\ &\quad + L'\frac{1}{k_{\mathrm{F}}^4}(\mathbf{q}_2^2\mathbf{q}_3^2 - (\mathbf{q}_2\cdot\mathbf{q}_3)^2) + \dots\big] && (292)\end{aligned}$$

where L' is a coefficient to be determined. Now from comparison of this equations with Eq.(287) we see that

$$4L_2^{(3)}(n_0) = \frac{2\pi^3}{k_{\mathrm{F}}^9}\left(\frac{73}{1200} - L'\right) = \frac{2}{27\pi^3 n_0^3}\left(\frac{73}{1200} - L'\right) \tag{293}$$

Svendsen and von Barth [6, 8] determined from a numerical calculation of the function $L_{\mathrm{x}}^{(3)}$ that $L' = -1.4L = -7L/5$ where $L = 73/1200$ is the first coefficient between brackets in the equation above. This then yields $73/1200 - L' = 73/500$ and

$$L_2^{(3)}(n_0) = \frac{1}{54\pi^3}\frac{73}{500}\frac{1}{n_0^3} = \frac{73}{27000\pi^3}\frac{1}{n_0^3} \tag{294}$$

From this we obtain by comparison to Eq.(282) the following gradient expansion for the exchange energy

$$\begin{aligned} E_{\mathrm{x}}[n] &= E_{\mathrm{x}}^{\mathrm{LDA}}[n] - \frac{5}{216\pi}\frac{1}{(3\pi^2)^{1/3}}\int d^3\mathbf{r}\,\frac{(\nabla n(\mathbf{r}))^2}{n(\mathbf{r})^{4/3}}\\ &\quad - \frac{73}{64800\pi^3}\int d^3\mathbf{r}\,\frac{(\nabla^2 n(\mathbf{r}))^2}{n(\mathbf{r})^2}\\ &\quad + \frac{73}{27000\pi^3}\int d^3\mathbf{r}\,\frac{(\nabla^2 n(\mathbf{r}))(\nabla n(\mathbf{r}))^2}{n(\mathbf{r})^3} + \dots && (295)\end{aligned}$$

VIII. GRADIENT EXPANSION OF TWO-POINT FUNCTIONS

A. The functional Taylor expansion

In the previous section we discussed the gradient expansion of the exchange-correlation energy. However, it turns out to be very useful in the construction of new functionals to also be able to find gradient expansions of two-point functions such as exchange-correlation holes, or the one-particle density matrix. Let us therefore consider an arbitrary two-poinf function $f[n](\mathbf{r},\mathbf{r}')$. This will have the following functional Taylor expansion around a given constant density n_0:

$$\begin{aligned} f[n](\mathbf{r},\mathbf{r}') &= f(n_0,|\mathbf{r}-\mathbf{r}'|)+ \\ &\sum_{m=1}^{\infty}\frac{1}{m!}\int d^{3m}\mathbf{r}\, M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m)\delta(\mathbf{r}_1)\ldots\delta n(\mathbf{r}_m) \end{aligned} \tag{296}$$

where we defined

$$M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m)=\frac{\delta^m f(\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}_1)\ldots\delta n(\mathbf{r}_m)}|_{n_0} \tag{297}$$

Since the function $M^{(m)}$ are evaluated at the homogeneous density n_0 the have the symmetry properties of the homogeneous electron gas. These symmetries are the same ones as for the functions K_{xc} discussed before i.e.

$$M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m) = M^{(m)}(n_0;\mathbf{r}+\mathbf{a},\mathbf{r}'+\mathbf{a},\mathbf{r}_1+\mathbf{a}\ldots\mathbf{r}_m+\mathbf{a}) \tag{298}$$

$$M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m) = M^{(m)}(n_0;R\mathbf{r},R\mathbf{r}',R\mathbf{r}_1\ldots R\mathbf{r}_m) \tag{299}$$

$$M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m) = M^{(m)}(n_0;-\mathbf{r},-\mathbf{r}',-\mathbf{r}_1,\ldots,-\mathbf{r}_m) \tag{300}$$

Since in Eq.(298) the vector $\mathbf{a}$ is arbitrary we can in particular choose $\mathbf{a}=-\mathbf{r}'$ and define

$$\begin{aligned} M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m) &= M^{(m)}(n_0;\mathbf{r}-\mathbf{r}',0,\mathbf{r}_1-\mathbf{r}',\ldots,\mathbf{r}_m-\mathbf{r}') \\ &\equiv N^{(m)}(n_0;\mathbf{r}-\mathbf{r}',\mathbf{r}_1-\mathbf{r}',\ldots,\mathbf{r}_m-\mathbf{r}') \end{aligned} \tag{301}$$

Then, as follows directly from the definition of the functions $M^{(m)}$ we also have the permutational symmetry

$$M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m)=M^{(m)}(n_0;\mathbf{r},\mathbf{r}',\mathbf{r}_{\pi(1)}\ldots\mathbf{r}_{\pi(m)}) \tag{302}$$

for all permutations π of the numbers $1\ldots m$. Our interest will be in the functions $N^{(m)}$ and in particular their Fourier transforms

$$N^{(m)}(\mathbf{r}-\mathbf{r}',\mathbf{q}_1\ldots\mathbf{q}_m)=\int d^3\mathbf{r}_1\ldots d^3\mathbf{r}_m\, N^{(m)}(n_0;\mathbf{r}-\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m)\, e^{-i\mathbf{q}_1\cdot\mathbf{r}_1-\ldots-i\mathbf{q}_m\cdot\mathbf{r}_m} \tag{303}$$

with Fourier inverse

$$N^{(m)}(n_0;\mathbf{r}-\mathbf{r}',\mathbf{r}_1\ldots\mathbf{r}_m)=\int\frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\, N^{(m)}(\mathbf{r}-\mathbf{r}',\mathbf{q}_1\ldots\mathbf{q}_m)e^{i\mathbf{q}_1\cdot\mathbf{r}_1+\ldots+i\mathbf{q}_m\cdot\mathbf{r}_m} \tag{304}$$

With these definitions we obtain

$$\begin{aligned} f[n](\mathbf{r},\mathbf{r}') &= f(n_0,|\mathbf{r}-\mathbf{r}'|)+ \\ &\sum_{m=1}^{\infty}\frac{1}{m!}\int d^{3m}\mathbf{r}\int\frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\, N^{(m)}(\mathbf{r}-\mathbf{r}',\mathbf{q}_1\ldots\mathbf{q}_m)e^{i\mathbf{q}_1\cdot(\mathbf{r}_1-\mathbf{r}')+\ldots+i\mathbf{q}_m\cdot(\mathbf{r}_m-\mathbf{r}')}\delta n(\mathbf{r}_1)\ldots\delta n(\mathbf{r}_m) \\ &= f(n_0,|\mathbf{r}-\mathbf{r}'|)+ \\ &\sum_{m=1}^{\infty}\frac{1}{m!}\int\frac{d^{3m}\mathbf{q}}{(2\pi)^{3m}}\, N^{(m)}(\mathbf{r}-\mathbf{r}',\mathbf{q}_1\ldots\mathbf{q}_m)e^{-i(\mathbf{q}_1+\ldots+\mathbf{q}_m)\cdot\mathbf{r}'}\delta n(-\mathbf{q}_1)\ldots\delta n(-\mathbf{q}_m) \end{aligned} \tag{305}$$

This is our first result. We further derive a consistency condition that is necessary for the existence of the gradient expansion. It follows directly from the definition of the functions $M^{(m)}$ that

$$\delta M^{(m)}(n_0; \mathbf{r}, \mathbf{r}', \mathbf{r}_1 \dots \mathbf{r}_m) = \int d^3\mathbf{r}''\, M^{(m+1)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}_1 \dots \mathbf{r}_m)\delta n(\mathbf{r}'') \tag{306}$$

taking $\delta n(\mathbf{r}'') = \delta n_0$ then yields.

$$\frac{\partial M^{(m)}}{\partial n_0}(n_0; \mathbf{r}, \mathbf{r}', \mathbf{r}_1 \dots \mathbf{r}_m) = \int d^3\mathbf{r}''\, M^{(m+1)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}_1 \dots \mathbf{r}_m) \tag{307}$$

If we translate this condition to $N^{(m)}$ then we obtain

$$\frac{\partial N^{(m)}}{\partial n_0}(n_0; \mathbf{y}, \mathbf{q}_1 \dots \mathbf{q}_m) = N^{(m+1)}(\mathbf{y}, 0, \mathbf{q}_1 \dots \mathbf{q}_m) \tag{308}$$

We our now ready to discuss the gradient expansion of $N^{(m)}$.

B. The gradient expansion

The function $N^{(m)}$ in Fourier space inherits the symmetry properties of $M^{(m)}$, i.e.

$$\begin{aligned}
N^{(m)}(n_0; \mathbf{y}, \mathbf{q}_1 \dots \mathbf{q}_m) &= M^{(m)}(n_0; R\mathbf{y}, R\mathbf{q}_1 \dots R\mathbf{q}_m) && (309)\\
N^{(m)}(n_0; \mathbf{y}, \mathbf{q}_1 \dots \mathbf{q}_m) &= M^{(m)}(n_0; -\mathbf{y}, -\mathbf{q}_1 \dots - \mathbf{q}_m) && (310)\\
N^{(m)}(n_0; \mathbf{y}, \mathbf{q}_1 \dots \mathbf{q}_m) &= M^{(m)}(n_0; \mathbf{y}, \mathbf{q}_{\pi(1)} \dots \mathbf{q}_{\pi(m)}) && (311)
\end{aligned}$$

where we denoted $\mathbf{y} = \mathbf{r} - \mathbf{r}'$. Similarly as in the previous section this implies that the functions $N^{(m)}$ can be expanded in symmetric polynomials (wrt to the $\mathbf{q}$ vectors) in the variables $\mathbf{y} \cdot \mathbf{y}$, $\mathbf{y} \cdot \mathbf{q}_i$ and $\mathbf{q}_i \cdot \mathbf{q}_j$. We therefore have the expansion

$$\begin{aligned}
&N^{(m)}(n_0; \mathbf{y}, \mathbf{q}_1 \dots \mathbf{q}_m) = \\
&\quad N_0^{(m)}(y) + N_1^{(m)}(y)\,\mathbf{y} \cdot \sum_{i=1}^{m} \mathbf{q}_i + N_2^{(m)}(y) \sum_{i=1}^{m} \mathbf{q}_i^2 + N_3^{(m)}(y) \sum_{i=1}^{m} (\mathbf{y} \cdot \mathbf{q}_i)^2 \\
&\quad + N_4^{(m)}(y) \sum_{i>j}^{m} (\mathbf{q}_i \cdot \mathbf{q}_j) + N_5^{(m)}(y) \sum_{i>j}^{m} (\mathbf{y} \cdot \mathbf{q}_i)(\mathbf{y} \cdot \mathbf{q}_j) + \dots
\end{aligned} \tag{312}$$

If we now use Eq.(308) the we see that

$$N_j^{(m+1)}(y) = \frac{\partial N_j^{(m)}}{\partial n_0}(y) \tag{313}$$

If we insert Eq.(312) into Eq.(305) and Fourier transform back to real space we see that

$$f[n](\mathbf{r}, \mathbf{r}') = f(n_0, |\mathbf{r} - \mathbf{r}'|) + \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{j=0}^{\infty} N_j^{(m)} A_j^{(m)} \tag{314}$$

where the first coefficients $A_j^{(m)}$ have the explicit form

$$
\begin{aligned}
A_0^{(m)} &= \delta n(\mathbf{r}')^m && (315)\\
A_1^{(m)} &= i\, m(\delta n(\mathbf{r}'))^{m-1}\, \mathbf{y}\cdot\nabla\delta n(\mathbf{r}') && (316)\\
A_2^{(m)} &= -m(\delta n(\mathbf{r}'))^{m-1}(\mathbf{y}\cdot\nabla)^2\delta n(\mathbf{r}') && (317)\\
A_3^{(m)} &= -m(\delta n(\mathbf{r}'))^{m-1}\,\nabla^2\delta n(\mathbf{r}') && (318)\\
A_4^{(m)} &= -\frac{1}{2}m(m-1)(\delta n(\mathbf{r}'))^{m-2}\,(\nabla\delta n(\mathbf{r}'))^2 && (319)\\
A_5^{(m)} &= -\frac{1}{2}m(m-1)(\delta n(\mathbf{r}'))^{m-2}\,(\mathbf{y}\cdot\nabla\delta n(\mathbf{r}'))^2 && (320)
\end{aligned}
$$

If we further use the condition Eq.(308) which tells us that

$$
\begin{aligned}
N_0^{(m)}(y) &= \frac{\partial^{(m)} f}{\partial n_0^m}(n_0; y) && (321)\\
N_i^{(m)}(y) &= \frac{\partial^{m-1} N_i^{(1)}}{\partial n_0^{m-1}}(n_0; y) \quad (i = 1,2,3) && (322)\\
N_i^{(m)}(y) &= \frac{\partial^{m-2} N_i^{(2)}}{\partial n_0^{m-2}}(n_0; y) \quad (i = 4,5) && (323)
\end{aligned}
$$

in Eq.(314) we obtain the expansion

$$
\begin{aligned}
& f[n](\mathbf{r},\mathbf{r}') = f(n_0, |\mathbf{r}-\mathbf{r}'|) + \\
& \quad \sum_{l=1}^{\infty} \frac{1}{l!}\frac{\partial^m f}{\partial n_0^m}(n_0; y)\delta n(\mathbf{r}')^l + \\
& \quad \sum_{l=1}^{\infty} \frac{1}{l!}\delta n(\mathbf{r}')^l \big[i\frac{\partial^l N_1^{(1)})}{\partial n_0^l}(\mathbf{y}\cdot\nabla\delta n(\mathbf{r}')) - \frac{\partial^l N_2^{(1)}}{\partial n_0^l}\nabla^2 n(\mathbf{r}') - i\frac{\partial^l N_3^{(1)}}{\partial n_0^l}(\mathbf{y}\cdot\nabla)^2 n(\mathbf{r}')\big] + \\
& \quad \sum_{l=1}^{\infty} \frac{1}{l!}\delta n(\mathbf{r}')^l \big[\frac{\partial^l N_4^{(2)}}{\partial n_0^l}(\nabla n(\mathbf{r}'))^2 + \frac{\partial^l N_5^{(2)}}{\partial n_0^l}(\mathbf{y}\cdot\nabla n(\mathbf{r}'))^2 \big] + \ldots \qquad (324)
\end{aligned}
$$

This can be resummed to finally give

$$
\begin{aligned}
& f[n](\mathbf{r},\mathbf{r}') = f(n(\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|) + \\
& \quad iN_1^{(1)}(n(\mathbf{r}'), y)\,\mathbf{y}\cdot\nabla n(\mathbf{r}') - N_2^{(1)}(n(\mathbf{r}'), y)\,\nabla^2 n(\mathbf{r}') - N_3^{(1)}(n(\mathbf{r}'), y)\,(\mathbf{y}\cdot\nabla)^2 n(\mathbf{r}') \\
& \quad -\frac{1}{2}N_4^{(2)}(n(\mathbf{r}'), y)\,(\nabla n(\mathbf{r}'))^2 - \frac{1}{2}N_5^{(2)}(n(\mathbf{r}'), y)\,(\mathbf{y}\cdot\nabla n(\mathbf{r}'))^2 + \ldots \qquad (325)
\end{aligned}
$$

We see that we have completely eliminated the dependence on the reference density n_0. To calculate the coefficients $N_1^{(1)}, N_2^{(1)}$ and $N_3^{(1)}$ we need to calculate the function $N^{(1)}(n_0; \mathbf{y}, \mathbf{q})$ and expand it in powers of $\mathbf{q}$:

$$
N^{(1)}(n_0; \mathbf{y}, \mathbf{q}) = N_0^{(1)}(n_0; y) + N_1^{(1)}(n_0; y)\mathbf{y}\cdot\mathbf{q} + N_2^{(1)}(n_0; y)\mathbf{q}^2 + N_3^{(1)}(n_0; y)(\mathbf{y}\cdot\mathbf{q})^2 + \ldots \qquad (326)
$$

The determination of the coefficients $N_4^{(2)}$ and $N_5^{(2)}$ requires knowledge of the function

$$
\begin{aligned}
N^{(2)}(n_0; \mathbf{y}, \mathbf{q}_1, \mathbf{q}_2) &= N_0^{(2)}(n_0; y) + N_1^{(2)}(n_0; y)\mathbf{y}\cdot(\mathbf{q}_1 + \mathbf{q}_2) \\
&\quad + N_2^{(2)}(n_0; y)(\mathbf{q}_1^2 + \mathbf{q}_2^2) + N_3^{(2)}(n_0; y)((\mathbf{y}\cdot\mathbf{q}_1)^2 + (\mathbf{y}\cdot\mathbf{q}_1)^2) \\
&\quad + N_4^{(2)}(n_0; y)(\mathbf{q}_1\cdot\mathbf{q}_2) + N_5^{(2)}(n_0; y)(\mathbf{y}\cdot\mathbf{q}_1)(\mathbf{y}\cdot\mathbf{q}_2) + \ldots \qquad (327)
\end{aligned}
$$

where the functions $N^{(1)}$ and $N^{(1)}$ are obtained from

$$\begin{aligned} \frac{\delta f(\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}'')} &= M^{(1)}(\mathbf{r},\mathbf{r}',\mathbf{r}'') = N^{(1)}(\mathbf{r}-\mathbf{r}',\mathbf{r}''-\mathbf{r}') && (328) \\ \frac{\delta f(\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}'')\delta n(\mathbf{r}''')} &= M^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''') = N^{(1)}(\mathbf{r}-\mathbf{r}',\mathbf{r}''-\mathbf{r}',\mathbf{r}'''-\mathbf{r}') && (329) \end{aligned}$$

If we take $f(\mathbf{r},\mathbf{r}') = \gamma_s[n](\mathbf{r},\mathbf{r}')$, i.e. the one-particle density matix of the Kohn-Sham system, then we find the expansion

$$\begin{aligned} \gamma_s[n](\mathbf{r},\mathbf{r}') &= \frac{1}{4\pi^2}\Big[4k_{\mathrm{F}}^3\frac{j_1(z)}{z} + \frac{1}{6}\frac{\nabla^2 k_{\mathrm{F}}^2}{k_{\mathrm{F}}}(j_0(z) - zj_1(z)) + \\ &+ \frac{1}{3}\frac{1}{k_{\mathrm{F}}}\Big(\nabla\cdot(\nabla k_{\mathrm{F}}^2\cdot\frac{\mathbf{y}}{y})\Big)\cdot\frac{\mathbf{y}}{y}\,z^2\,j_0(z) + \nabla k_{\mathrm{F}}^2\cdot\frac{\mathbf{y}}{y}\,zj_0(z) \\ &- \frac{1}{24}\frac{(\nabla k_{\mathrm{F}}^2)^2}{k_{\mathrm{F}}^3}(j_0(z)(1+z^2) - zj_1(z)) \\ &+ \frac{1}{8}\frac{1}{k_{\mathrm{F}}^3}\Big(\nabla k_{\mathrm{F}}^2\cdot\frac{\mathbf{y}}{y})\Big)^2(z^2j_0(z) - z^3j_1(z))\Big] && (330) \end{aligned}$$

where $k_{\mathrm{F}} = (3\pi^2 n(\mathbf{r}'))^{1/3}$ and $z = k_{\mathrm{F}}(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|$.

IX. GENERALIZED GRADIENT APPROXIMATIONS

A. The gradient expansion of the exchange hole

Let us now study the gradient expansion of the exchange-hole. We follow the work of J.Perdew [9] For a spin-compenstaed system the pair-correlation function is given by

$$g_{\mathrm{x}}(\mathbf{r},\mathbf{r}') = 1 - \frac{1}{2}\frac{|\gamma_s(\mathbf{r},\mathbf{r}')|^2}{n(\mathbf{r})n(\mathbf{r}')} \tag{331}$$

We therefore obtain for the exchange hole the expression

$$n_{\mathrm{x}}(\mathbf{r}'|\mathbf{r}) = n(\mathbf{r}')(g_{\mathrm{x}}(\mathbf{r},\mathbf{r}') - 1) = -\frac{1}{2n(\mathbf{r})}|\gamma_s(\mathbf{r},\mathbf{r}')|^2 \tag{332}$$

For the special case $\mathbf{r} = \mathbf{r}'$ we obtain the following value for the on-top hole

$$n_{\mathrm{x}}(\mathbf{r}|\mathbf{r}) = -\frac{1}{2}n(\mathbf{r}) \tag{333}$$

We can now insert in Eq.(332) the gradient expansion of the one-particle density matrix γ_s of Eq.(330). This gives the so-called Gradient Expansion Approximation (GEA) of the exchange hole. In view of Eq.(333) this is conveniently written as.

$$n_{\mathrm{x}}^{\mathrm{GEA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) = -\frac{1}{2}n(\mathbf{r})y(\mathbf{r},\mathbf{u}) \tag{334}$$

where we defined $\mathbf{u} = \mathbf{r}' - \mathbf{r}$ and

$$\begin{aligned} y(\mathbf{r},\mathbf{u}) &= J + L\hat{u}\frac{\nabla k_{\mathrm{F}}^2}{k_{\mathrm{F}}^2} + (z^2J - 4zL)\frac{(\nabla k_{\mathrm{F}}^2)^2}{192k_{\mathrm{F}}^6} \\ &+ M\frac{(\hat{u}\cdot\nabla k_{\mathrm{F}}^2)^2}{k_{\mathrm{F}}^6} - z^2J\frac{\nabla^2 k_{\mathrm{F}}^2}{48k_{\mathrm{F}}^4} + zL\frac{(\hat{u}\cdot\nabla)^2 k_{\mathrm{F}}^2}{6k_{\mathrm{F}}} && (335) \end{aligned}$$

where $\hat{u} = \mathbf{u}/u$, $u = |\mathbf{u}|$ and $k_{\mathrm{F}}(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}$. The functions J, L and M are functions of $z = 2k_{\mathrm{F}}(\mathbf{r})u$ and have the explicit form

$$J(z) = \frac{72}{z^6}(4 - 4\cos z - 4z\sin z + z^2 + z^2\cos z) \tag{336}$$

$$L(z) = \frac{9}{z^3}(2 - 2\cos z - z\sin z) \tag{337}$$

$$M(z) = \frac{9}{16z}(\sin z - z\cos z) \tag{338}$$

The main observation by Perdew was that the GEA exchange hole violates the following exact conditions

$$n_{\mathrm{x}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) \leq 0 \tag{339}$$

$$\int d^3\mathbf{u}\, n_{\mathrm{x}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) = -1 \tag{340}$$

The main idea was therefore to enforce these constraints on the GEA hole by means of a cutoff procedure. This leads to what is known as the Generalized Gradient Approximation (GGA) with exchange hole

$$n_{\mathrm{x}}^{\mathrm{GGA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) = -\frac{1}{2}n(\mathbf{r})y(\mathbf{r},\mathbf{u})\theta(y(\mathbf{r},\mathbf{u}))\theta(R(\mathbf{r}) - u) \tag{341}$$

where θ is the Heaviside function $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ otherwise. This ensures that the hole function is negative always. The last θ-function in Eq.(341) cuts off the hole at a radius $R(\mathbf{r})$. This radius is determined by the requirement that the sumrule Eq.(340) for the exchange hole is satisfied:

$$\int d^3\mathbf{u}\, n_{\mathrm{x}}^{\mathrm{GGA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) = -1 \tag{342}$$

This procedure led to a considerable improvement of the exchange energies without the need of empirical parameters. The procedure was, however, somewhat complicated for actual applications. Therefore Perdew and Wang [10] published a simplified method. The first step in this scheme consists of the observation that the GEA expression for the exchange energy

$$E_{\mathrm{x}}^{\mathrm{GEA}}[n] = \frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{u}\frac{n(\mathbf{r})n_{\mathrm{x}}^{\mathrm{GEA}}(\mathbf{r}+\mathbf{u}|\mathbf{r})}{|\mathbf{u}|} \tag{343}$$

can by means of partial integration also be written as

$$E_{\mathrm{x}}^{\mathrm{GEA}}[n] = \frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{u}\frac{n(\mathbf{r})\tilde{n}_{\mathrm{x}}^{\mathrm{GEA}}(\mathbf{r}+\mathbf{u}|\mathbf{r})}{|\mathbf{u}|} \tag{344}$$

where the function $\tilde{n}_{\mathbf{x}}^{\mathrm{GEA}}$ now only depends of first order derivatives of the density. The explicit form is given by

$$\tilde{n}_{\mathbf{x}}^{\mathrm{GEA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) = -\frac{1}{2}n(\mathbf{r})\tilde{y}(\mathbf{r},\mathbf{u}) \tag{345}$$

where

$$\tilde{y}(\mathbf{r},\mathbf{u}) = J + \frac{4}{3}L\hat{u}\cdot\mathbf{s} - \frac{16}{27}M(\hat{u}\cdot\mathbf{s})^2 - \frac{16}{3}N\, s^2 \tag{346}$$

where

$$\mathbf{s}(\mathbf{r}) = \frac{\nabla n(\mathbf{r})}{2k_{\mathrm{F}}(\mathbf{r})n(\mathbf{r})} \tag{347}$$

and $s = |\mathbf{s}|$. The function N is defined as

$$N(z) = \frac{3}{16z^4}[8 - (8 - 4z^2)\cos z - (8z - z^3)\sin z] \tag{348}$$

where $z = 2k_{\mathrm{F}}u$. The function $\tilde{n}_{\mathbf{x}}^{\mathrm{GEA}}$ can now not be interpreted as an exchange hole. However, the quantities

$$\begin{aligned} \langle n_{\mathrm{x}}^{\mathrm{GEA}}(\mathbf{u})\rangle &= \frac{1}{N}\int d^3\mathbf{r}\, n(\mathbf{r})n_x^{\mathrm{GEA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) \\ &= \frac{1}{N}\int d^3\mathbf{r}\, n(\mathbf{r})\tilde{n}_x^{\mathrm{GEA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) \\ &= \langle \tilde{n}_{\mathrm{x}}^{\mathrm{GEA}}(\mathbf{u})\rangle \end{aligned} \tag{349}$$

are the same. These quantities have been called the system-averaged exchange holes. The exact system averaged exchange hole satisfies

$$\begin{aligned} \int d^3\mathbf{u}\langle n_{\mathrm{x}}(\mathbf{u})\rangle &= \frac{1}{N}\int d^3\mathbf{u}\, n(\mathbf{r})n_{\mathrm{x}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) \\ &= -\frac{1}{N}d^3\mathbf{r}\, n(\mathbf{r}) = -1 \end{aligned} \tag{350}$$

and

$$E_{\mathrm{x}}[n] = \frac{1}{2}\int d^3\mathbf{u}\,\frac{\langle n_{\mathrm{x}}(\mathbf{u})\rangle}{|\mathbf{u}|} \tag{351}$$

We see that the exchange energy only depends on the system averaged exchange hole, which also satisfies a sumrule. The idea of Perdew and Wang was to apply the real-space cutoff procedure to the exchange hole $\tilde{n}_{\mathbf{x}}^{\mathrm{GEA}}$, i.e. they write

$$n_{\mathrm{x}}^{\mathrm{GGA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) = -\frac{1}{2}n(\mathbf{r})\tilde{y}(\mathbf{r},\mathbf{u})\theta(\tilde{y}(\mathbf{r},\mathbf{u}))\theta(R(\mathbf{r}) - u) \tag{352}$$

The cutoff radius is again determined from the sumrule for the exchange hole. We have the following determining equation for this radius

$$\begin{aligned} -1 &= \int d^3\mathbf{u}\, n_{\mathrm{x}}^{\mathrm{GGA}}(\mathbf{r}+\mathbf{u}|\mathbf{r}) \\ &= -\frac{1}{2}n(\mathbf{r})\int du\, 4\pi u^2 \int \frac{d\Omega_{\mathbf{u}}}{4\pi}\,\tilde{y}(\mathbf{r},\mathbf{u})\theta(\tilde{y}(\mathbf{r},\mathbf{u}))\theta(R(\mathbf{r}) - u) \end{aligned} \tag{353}$$

where $d\Omega_{\mathbf{u}}$ denotes the integration over angular variables. The latter integral can be worked out as follows. We write

$$\tilde{y}(\mathbf{r},\mathbf{u}) = A + B\mu + C\mu^2 \tag{354}$$

where

$$\mu = \frac{\hat{u}\cdot\mathbf{s}}{|\mathbf{s}|} = \cos\theta \tag{355}$$

where θ is the angle between vectors $\hat{u}$ and $\mathbf{s}$. and we defined

$$\begin{aligned} A &= J - \frac{16}{3}Ns^2 && (356)\\ B &= \frac{4}{3}Ls && (357)\\ C &= -\frac{16}{27}Ms^2 && (358)\end{aligned}$$

Then

$$\begin{aligned}&\int \frac{d\Omega_{\mathbf{u}}}{4\pi}\,\tilde{y}(\mathbf{r},\mathbf{u})\theta(\tilde{y}(\mathbf{r},\mathbf{u}))\theta(R(\mathbf{r})-u) = \theta(R(\mathbf{r})-u)\frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta\,\sin\theta\,\tilde{y}\theta(\tilde{y})\\ &= \frac{1}{2}\theta(R(\mathbf{r})-u)\int_{-1}^{1} d\mu\,(A+B\mu+C\mu^2)\theta(A+B\mu+C\mu^2)\\ &= \theta(R(\mathbf{r})-u)g(2k_{\mathrm{F}}u,s) && (359)\end{aligned}$$

where we defined

$$g(2k_{\mathrm{F}}u,s) = \frac{1}{2}\int_{-1}^{1} d\mu\,(A+B\mu+C\mu^2)\theta(A+B\mu+C\mu^2) \tag{360}$$

where the coefficients A, B and C are functions of $2k_{\mathrm{F}}u$ and s. The sumrule becomes

$$\begin{aligned} -1 &= -\frac{1}{2}n(\mathbf{r})\int du\,4\pi u^2\,\theta(R(\mathbf{r})-u)\,g(2k_{\mathrm{F}}u,s)\\ &= -\frac{1}{2}n(\mathbf{r})\int_0^R du\,4\pi u^2\,g(2k_{\mathrm{F}}u,s)\\ &= -\frac{1}{2}n(\mathbf{r})\frac{4\pi}{(2k_{\mathrm{F}})^3}\int_0^{z_c} dz\,z^2\,g(z,s)\\ &= -\frac{n(\mathbf{r})\pi}{4(3\pi^2)n(\mathbf{r})}\int_0^{z_c} dz\,z^2\,g(z,s) = -\frac{1}{12\pi}\int_0^{z_c} dz\,z^2\,g(z,s) && (361)\end{aligned}$$

where we defined $z_c = 2k_F R$. This equation determines $z_c(s)$ as a function of s. The exchange energy then becomes

$$\begin{aligned} E_{\mathrm{x}}^{\mathrm{GGA}}[n] &= \frac{1}{2}\int d^3\mathbf{r}n(\mathbf{r})\int d^3\mathbf{u}\,\frac{n_{\mathrm{x}}^{\mathrm{GGA}}(\mathbf{r}+\mathbf{u}|\mathbf{r})}{|\mathbf{u}|}\\ &= \frac{1}{2}\int d^3\,n(\mathbf{r})\int du\,4\pi u^2\,\frac{1}{u}\int\frac{d\Omega_{\mathbf{u}}}{4\pi}n_{\mathrm{x}}^{\mathrm{GGA}}(\mathbf{r}+\mathbf{u}|\mathbf{r})\\ &= -\frac{1}{4}\int d^3\mathbf{r}\,n(\mathbf{r})^2\int_0^R du\,4\pi u\,g(z,s)\\ &= -\frac{1}{4}\int d^3\mathbf{r}\,n(\mathbf{r})^2\,\frac{4\pi}{(2k_{\mathrm{F}})^2}\int_0^{z_c} dz\,z\,g(z,s)\\ &= -\frac{\pi}{4(3\pi^2)^{2/3}}\int d^3\mathbf{r}\,n^{4/3}(\mathbf{r})\int_0^{z_c} dz\,z\,g(z,s)\\ &= A_{\mathbf{x}}\int d^3\mathbf{r}\,n^{4/3}(\mathbf{r})F(s) && (362)\end{aligned}$$

where we defined

$$F(s) = -\frac{(3\pi^2)^{1/3}}{12\pi A_{\mathrm{x}}}\int_0^{z_c(s)} dz\,z\,g(z,s) \tag{363}$$

and $A_{\mathrm{x}} = -(3/4)(3/\pi)^{1/3}$ is the coefficient of the LDA exchange functional. When $s \to 0$ then the GEA exchange hole becomes equal to the LDA exchange hole and consequently $z_c \to \infty$ and $F(s = 0) = 1$. On the other hand, for $s \to \infty$ the hole radius $z_c \to 0$. The function $F(s)$ can be evaluated numerically. Perdew and Wang fitted the numerical result to the following expression

$$F(s) = (1 + \frac{a}{m} s^2 + b s^4 + c s^6)^m \tag{364}$$

where $a = 7/81, b = 14, c = 1/5$ and $m = 1/15$. The coefficient a was chosen in order to make sure that the GGA exchange energy functional would reduce to the GEA one for slowly varying densities. However, Perdew and Wang based their work on a calculation of an exchange coefficient (by Sham) that turned out to be wrong (the correct value is $a = 10/81$). This has been repaired in later GGA fits derived in the same spirit.

B. Generalized gradient expansions for correlation

The generalized gradient expansion for correlation has been based on the same philosophy as for exchange. In this case we require the sumrule for the correlation hole to be satisfied i.e.

$$\int d^3u \, \bar{n}_{\mathrm{c}}(\mathbf{r} + \mathbf{u}|\mathbf{r}) = 0 \tag{365}$$

and this time there is no negativity constraint. The analysis of the gradient expansion for the correlation hole is rather involved. Details can be found in the work of Langreth and Perdew [11] and is based on many-body Green function techniques. Wellknown GGA functionals for correlation are the modified Langreth-Mehl expression [12] and the PW91 correlation functional [2, 13].

C. The Becke exchange functional

The starting point for the derivation of a gradient functional by Becke [**?**] was quite different from that of Perdew. He started out be writing the exchange functional as

$$E_{\mathrm{x}}^{\mathrm{GGA}}[n] = E_{\mathrm{x}}^{\mathrm{LDA}}[n] + \int d^3r \, n^{4/3}(\mathbf{r}) \, f(x(\mathbf{r})) \tag{366}$$

where

$$x(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{n^{4/3}(\mathbf{r})} \tag{367}$$

(this is up to a prefactor the same quantity as Perdew's function $s(\mathbf{r})$). The functional then automatically satisfies the correct scaling properties of the exchange functional

$$\begin{aligned} E_{\mathrm{x}}[n_\lambda] &= \lambda E_{\mathrm{x}}[n] && (368) \\ n_\lambda(\mathbf{r}) &= \lambda^3 n(\lambda \mathbf{r}) && (369) \end{aligned}$$

The function $f(x)$ is then determined to satisfy two requirements. The first requirement that for small values of x the functional should reduce to the GEA form, i.e.

$$E_{x}^{\mathrm{GGA}}[n] \approx E_{\mathrm{x}}^{\mathrm{LDA}}[n] - \beta \int d^3\mathbf{r} \, \frac{(\nabla n(\mathbf{r}))^2}{n^{4/3}(\mathbf{r})} \tag{370}$$

This implies that

$$f(x) \approx -\beta x^2 \qquad (x \to 0) \tag{371}$$

The second requirement is that the correct form of exchange energy density in the outer region of atoms and molecules should be repropduced. From the expression for $E_{\mathrm{x}}[n]$ we see that the exchange energy functional is of the form

$$E_{\mathrm{x}}[n] = \int d^3r\, n(\mathbf{r})\epsilon_{\mathrm{x}}(\mathbf{r}) \tag{372}$$

where the exchange energy density is defined as

$$\epsilon_{\mathrm{x}}(\mathbf{r}) = \frac{1}{2}\int d^3r'\, \frac{n_{\mathrm{x}}(\mathbf{r}'|\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \tag{373}$$

Now for $|\mathbf{r}'| \to \infty$ we obtain

$$\epsilon_{\mathrm{x}}(\mathbf{r}) = \frac{1}{2|\mathbf{r}|}\int d^3r'\, n_{\mathrm{x}}(\mathbf{r}'|\mathbf{r}) = -\frac{1}{2|\mathbf{r}|} \qquad (|\mathbf{r}| \to \infty) \tag{374}$$

where the last step follows from the fact that exchange hole integrates to -1. We now want to choose the function $f(x)$ in such a way that this behavior is reproduced. Now for a finite system the density decays asymptotically as $n(\mathbf{r}) = Ce^{-\alpha r}$ where $r = |\mathbf{r}| \to \infty$. We then have that

$$|\nabla n(\mathbf{r})| = |-\alpha\frac{\mathbf{r}}{|\mathbf{r}|}Ce^{-\alpha r}| = \alpha n(\mathbf{r}) \qquad (r \to \infty) \tag{375}$$

and therefore

$$x(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{n^{4/3}(\mathbf{r})} = \alpha n(\mathbf{r})^{-1/3} = \alpha C^{-1/3}e^{\alpha r/3} \qquad (r \to \infty) \tag{376}$$

and therefore that

$$\ln x \approx \frac{1}{3}\alpha r \qquad (r \to \infty) \tag{377}$$

From this relation we then deduce that

$$-\frac{1}{6}\frac{x}{\ln x} = -\frac{\alpha n^{-1/3}}{2\alpha r} = -\frac{n^{-1/3}}{2r} \qquad (r \to \infty) \tag{378}$$

For exponentially decaying densities $r \to \infty$ implies that $x \to \infty$. We thus see that if we require from the function $f(x)$ that

$$f(x) \approx -\frac{1}{6}\frac{x}{\ln x} \qquad (x \to \infty) \tag{379}$$

then

$$n^{4/3}(\mathbf{r})f(x) \to -\frac{n(\mathbf{r})}{2r} \tag{380}$$

and we then require the correct asymptotic form of the exchange energy density. Conditions Eq.(216) and (218) are incorporated in the following parametrization

$$f(x) = -\frac{\beta x^2}{1+6\beta x \sinh^{-1} x} \tag{381}$$

Finally Becke fitted the parameter β to obtain the exact exchange energy of the noble gas atoms. This yielded a value of $\beta = 0.0042$. Therefore the final Becke GGA for exchange is given by

$$E_x^{\mathrm{GGA}}[n] = E_{\mathrm{x}}^{\mathrm{LDA}}[n] - \beta \int d^3r \, \frac{x^2}{1 + 6\beta x \sinh^{-1} x} \tag{382}$$

This functional [14] is also known as the B88 functional. The functional has been very successful in improving the bond energies of molecules.

X. CLIMBING THE DENSITY-FUNCTIONAL LADDER: THE META-GGA

XI. SPIN DENSITY FUNCTIONAL THEORY

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